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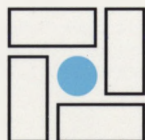
LITHOLOGY AND MINERAL RESOURCES

Official English Translation of *Litologiya i Poleznye Iskopaemye*

Editor-in-Chief
Vladimir N. Kholodov

Academician of the Academy of Natural Sciences
Professor, Doctor of Geology and Mineralogy

**A Journal on Problems of the Theory of
Sedimentary Rock Formation and Ore Genesis**



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Lithology and Mineral Resources

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Lithology and Mineral Resources (Litologiya i Poleznye Iskopaemye) reviews a wide range of problems related to the formation of sedimentary rocks and ores. Special attention is devoted to comparison of ancient sedimentary rock- and ore formation with present-day processes, as the idea of actualism has always constituted one of the bases of the scientific philosophy of lithologists. A major part of the journal is devoted to comparative analysis of sedimentary processes on continents and in oceans, as well as the genetic aspects of the formation of sedimentary and hydrothermal-sedimentary mineral resources. The journal was founded in 1963 by Academician N. M. Strakhov. It will be of interest to lithologists, petrographers, geochemists, mineralogists, ore geologists and metallogenists, as well as to other geologists, ecologists, researchers of experimental and analytical laboratories, and graduate students.

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Shallowing-Upward Cycles in the Lower Paleozoic Shallow-Marine Carbonates of Malyi Karatau, Kazakhstan

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Abstract—The Cambrian–Ordovician deposits of the Lower Paleozoic Aisha-Bibi carbonate platform in the Malyi Karatau region consist of a variety of facies related to depositional environments ranging from basin plain to tidal flat. Significant portions of the shallow-marine sections are represented by stacks of meter-scale shallowing-upward cycles. The typical cycle consists of (from bottom to top) transgressive lag flat-pebble conglomerates, subtidal cross-stratified and bioturbated grainstones and mudstones of sand shoals and lagoons, thrombolites representing patch reefs, intertidal “ribbon rocks,” and upper intertidal-supratidal mudcracked laminites and stromatolites. The prevalent stacking of cycles indicates that repeating changes of depositional environments occurred. These changes are attributed to high-frequency oscillations of relative sea level affecting deposition. It is suggested that these sea level changes have most likely been related to Milankovitch astronomical rhythms.

INTRODUCTION

Sequences of shallowing-upward cycles are well-known in shallow-marine deposits of carbonate platforms around the world from the Phanerozoic. However, the origin of cyclicity in such deposits is not yet entirely understood. A significant part of the Lower Paleozoic Shabakty Series of Malyi Karatau is composed of cyclic shallow-marine carbonates (Cook *et al.*, 1991, and others). Numerous superb outcrops allow for detailed description of these sections. In addition, the large-scale facies structure of the unique Lower Paleozoic Aisha-Bibi seamount has been analyzed and described by Cook and others (Cook and Taylor, 1990; Cook *et al.*, 1991; Cook *et al.*, 1989). The objective of this paper is to describe and analyze the shallowing-upward peritidal cycles of Aisha-Bibi, describe and interpret all subfacies composing these cycles, and explore the basic role of sea level changes in the formation of cycles.

GEOLOGICAL SETTING

The Lower Paleozoic rocks of Malyi Karatau are exposed along a stretch about 100 km long and 20 km wide (Fig. 1). They are stratigraphically underlain by Vendian siliciclastic and volcanoclastic deposits and unconformably overlain by Upper Devonian and Lower Carboniferous siliciclastics and carbonates. Internally, the Lower Paleozoic of Malyi Karatau is composed of the Lower Cambrian Chulaktau Series (dolomites, phosphates, chert; thickness under 75 m), Lower Cambrian–Middle Ordovician Shabakty Series (limestones and dolomites, 1500 to 3000 m thick), and, locally, the Middle Ordovician Zhyrykauz Series (siliciclastics and minor amounts of limestones, up to 530 m thick)

(Abdulin *et al.*, 1986) (Fig. 2). Only the deposits of the Shabakty Series are included in the scope of this paper.

The stratigraphy and paleontology of the Shabakty Series have been studied by numerous workers (Abdulin *et al.*, 1990; Apollonov *et al.*, 1983, 1984; Apollonov and Zhemchuzhnikov, 1988; Dubinina, 1991; Ergaliev, 1980, 1981, 1989; Sovetov, 1990; Zhemchuzhnikov, 1986; Zhemchuzhnikov *et al.*, 1989). On the basis of an integrated analysis of sedimentologic, paleontologic, and structural data, Cook and co-workers interpreted the depositional setting of the Lower Paleozoic carbonates of Malyi Karatau as an isolated carbonate platform, the Aisha-Bibi seamount (Cook and Taylor, 1990; Cook *et al.*, 1991, 1989) (Fig. 3). The Aisha-Bibi seamount is believed to be about 40 km wide. It is believed that the Aisha-Bibi platform formed as one of a number of isolated blocks during the Rhiphean–Vendian rifting of continental crust (Abdulin *et al.*, 1986; Ilyin, 1990; Sargaskaev, 1988, 1990) and became a site of Lower Paleozoic carbonate deposition (Cook and Taylor, 1990; Cook *et al.*, 1991, 1989).

Cook *et al.* (1991, 1989) and Cook and Taylor (1990) outlined a general picture of carbonate accumulation on the Aisha-Bibi seamount and described the main sedimentary facies and depositional environments. Facies identified by them range from seamount margin and interior to seamount slope and basin-plain facies. In addition, Cambrian–Early Ordovician limestones and shales of the Botakara Series of the adjacent Kokzhot Zone, described by Sargaskaev and Ergaliev (Sargaskaev, 1988, 1990; Sargaskaev and Ergaliev, 1988), also are thought to represent basin plain and fan fringe facies. Although most of the best explored sections are composed of relatively deep-water (platform

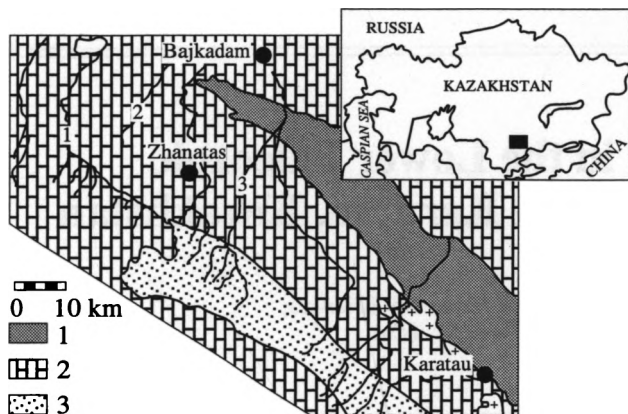


Fig. 1. Study area location map (modified from Kholodov and Koryakin, 1963). Measured sections: (1) Upper Paleozoic (Ooshbas), (2) Lower Paleozoic (Kok-Soo), (3) Proterozoic (Aktoogai).

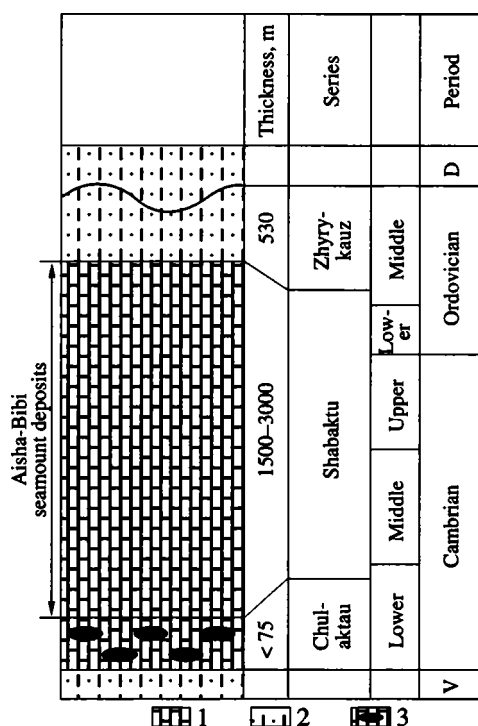


Fig. 2. Generalized stratigraphic column for Lower Paleozoic strata of the Malyy Karatau. (1) Limestones and dolomites; (2) sandstones and siltstones; (3) phosphorites and dolomites.

the subfacies composing these peritidal cycles and their respective paleoenvironmental interpretations follow.

SHALLOWING-UPWARD CYCLES OF AISHA-BIBI

Three uninterrupted well-exposed sections composed of shallow-marine carbonates of the Lower Cambrian–Middle Ordovician Shabakty Series were examined in detail during the field seasons of 1994 and 1995 (Fig. 1). The Ooshbas Section was measured on the western side of the Ooshbas Creek at 43°38'55"N, 69°15'62"E. The total thickness of the measured section is 275 m. The section is composed of 124 peritidal cycles ranging in thickness from 0.27 to 7.05 m; average thickness of a cycle is 2.22 m. The Aktoogai Section was measured on the western side of Shabakty Creek at 43°29'30"N, 69°51'61"E. The total thickness of this measured section is 256 m; it is composed of 48 cycles (0.82 to 39.7 m thick, average 5.26 m). The Kok-Soo Section was measured on the western side of Kok-Soo Creek at 43°39'95"N, 69°38'76"E. The thickness of the measured cyclic interval of this section is about 300 m. It is composed of 28 cycles from 1.05 to 32.7 m thick; the average thickness of a cycle is 10.7 m.

Although there are some variations in cycle composition, the general character of the cyclicity is the same for all sections. A segment of the measured cyclic section and a modal peritidal cycle are shown in Fig. 3. Each cycle consists of several distinct subfacies. The term "subfacies" will be used in this paper as per definition of Hardie (Hardie and Shinn, 1986), i.e., as a rock record of a subenvironment. Each of the subfacies has a unique set of characteristics which are described in detail below along with an interpretation of its depositional subenvironment. Within each cycle, the subfacies are arranged in a specific order. In the base of the cycle there is the flat-pebble conglomerate subfacies, overlain by the cross-stratified grainstone subfacies, which, in turn, grades up into the "ribbon rocks" subfacies and the laminite subfacies. Internal boundaries within a cycle are generally gradational, whereas the boundaries between the cycles are sharp and commonly erosional. It is argued that each cycle records deposition under shallowing-upward conditions—from shallow subtidal to supratidal. Below, the composition, sedimentary structures, and environmental interpretations are discussed for each of the subfacies mentioned above.

BASAL FLAT-PEBBLE CONGLOMERATE SUBFACIES

Description

The basal flat-pebble conglomerate subfacies does not comprise a large volume of any of the described sections, but it is nonetheless very important for determining the character of the cycles and cycle boundaries in particular. Basal conglomerates occur exclusively

margin and deeper) facies, others are composed of shallow-marine carbonates.

It is these shallow-marine facies that are the subject of the present study. They are well exposed in several sections across the platform. Most of the shallow-marine carbonates are dolomitized. Significant intervals within these sections are composed of stacks of peritidal shallowing-upward cycles. The description of

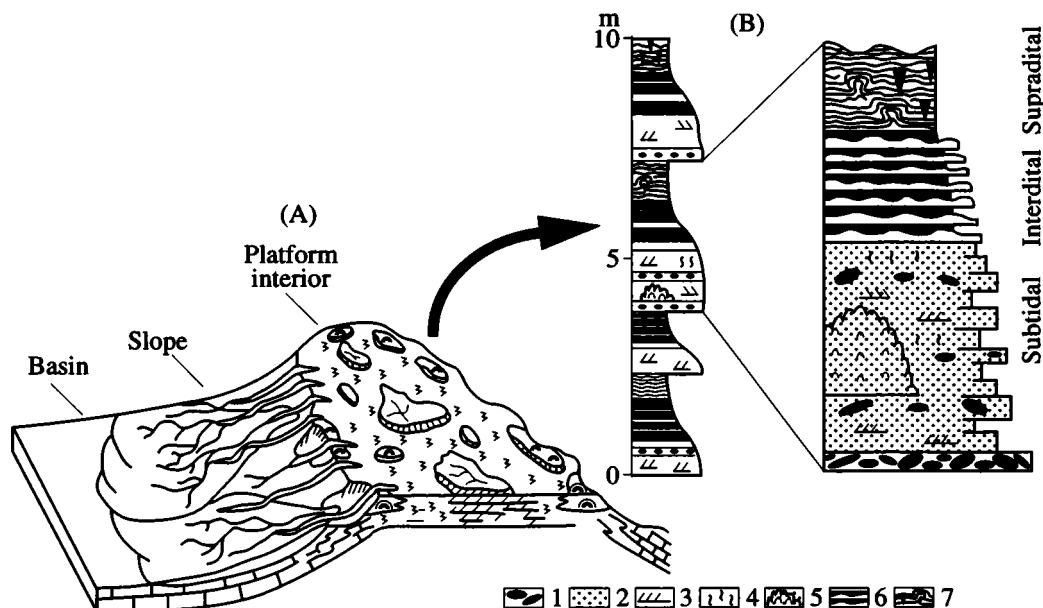


Fig. 3. (A) Block-diagram of the Aisha-Bibi platform (modified from Cook *et al.*, 1989); (B) portion of measured cyclic section from the platform interior and a modal shallowing-upward cycle. (1) Flat-pebble conglomerates; (2) grainstones; (3) cross-stratification; (4) traces of bioturbation; (5) thrombolites; (6) ribbon rocks; (7) mudcracked laminites and stromatolites.

within a few centimeters to a few tens of centimeters above the lower boundary of a cycle (Fig. 5b). They are characterized by intraclasts embedded in a matrix of grainstones or mudstones (see below). The intraclasts are typically elongated (discoid) and are usually 1 to 20 cm long; the thicknesses of the intraclasts range from a few millimeters to a few centimeters. Intraclasts characteristically have sharp angular edges and are not rounded. Within the grainstone matrix, they are commonly positioned either parallel to, or at low angle (usually not more than 20°) to the bedding plane. In some cases, intraclasts are positioned on the foresets of grainstone cross-beds. It is not unusual to find intraclasts that are bent slightly (which indicates that they were not lithified at the time of deposition).

The internal structure and texture of the intraclasts are identical to those of the underlying laminites (see below). They are composed of sub-millimeters to millimeters scale interlayering of mudstone and peloidal grainstone and are clearly internally laminated. The character of the lamination (parallel or, more commonly, wavy) is identical to that of the laminites. These intraclasts clearly have been eroded from the underlying laminites, most likely by the action of the currents that produced cross-stratification in the host grainstones. In a number of cases, it is possible to trace a single intraclast to its place of origin on the upper boundary of the laminite unit. Moreover, in some cases, the intraclasts are still partly attached to the laminites below, literally "caught in the act."

Interpretation

The features of the basal flat-pebble conglomerate sub-facies have major implications for understanding the nature of cyclicity of shallow-water deposits of the Aisha-Bibi seamount in general. The sharp, and in many cases, erosional boundaries between the laminites at the top of the underlying cycle (see below) and the overlying basal flat-pebble conglomerates and cross-stratified grainstone subfacies reflect abrupt changes of the environment, from supratidal to high-energy subtidal. The basal conglomerates clearly mark a transgression at the base of a cycle (transgressive lag conglomerates) and the beginning of a new cycle. In summary, basal flat-pebble conglomerates were deposited during the earliest stages of subtidal deposition of a cycle and are composed of intraclasts torn off the underlying laminites in a subtidal grainstone matrix.

CROSS-STRATIFIED GRAINSTONE SUBFACIES

Description

The subfacies comprised of cross-stratified grainstones is a major component in most of the cycles of the Ooshbas and Aktoogai sections. Cross-stratified grainstones are somewhat less common in the Kok-Soo Section.

Complete dolomitization makes it impossible to characterize the original mineralogical composition of the grainstones, but the replacement is largely fabric retentive so that primary depositional textures and structures can be determined. Internally, the cross-stratified grainstones appear to have a grain-supported fab-

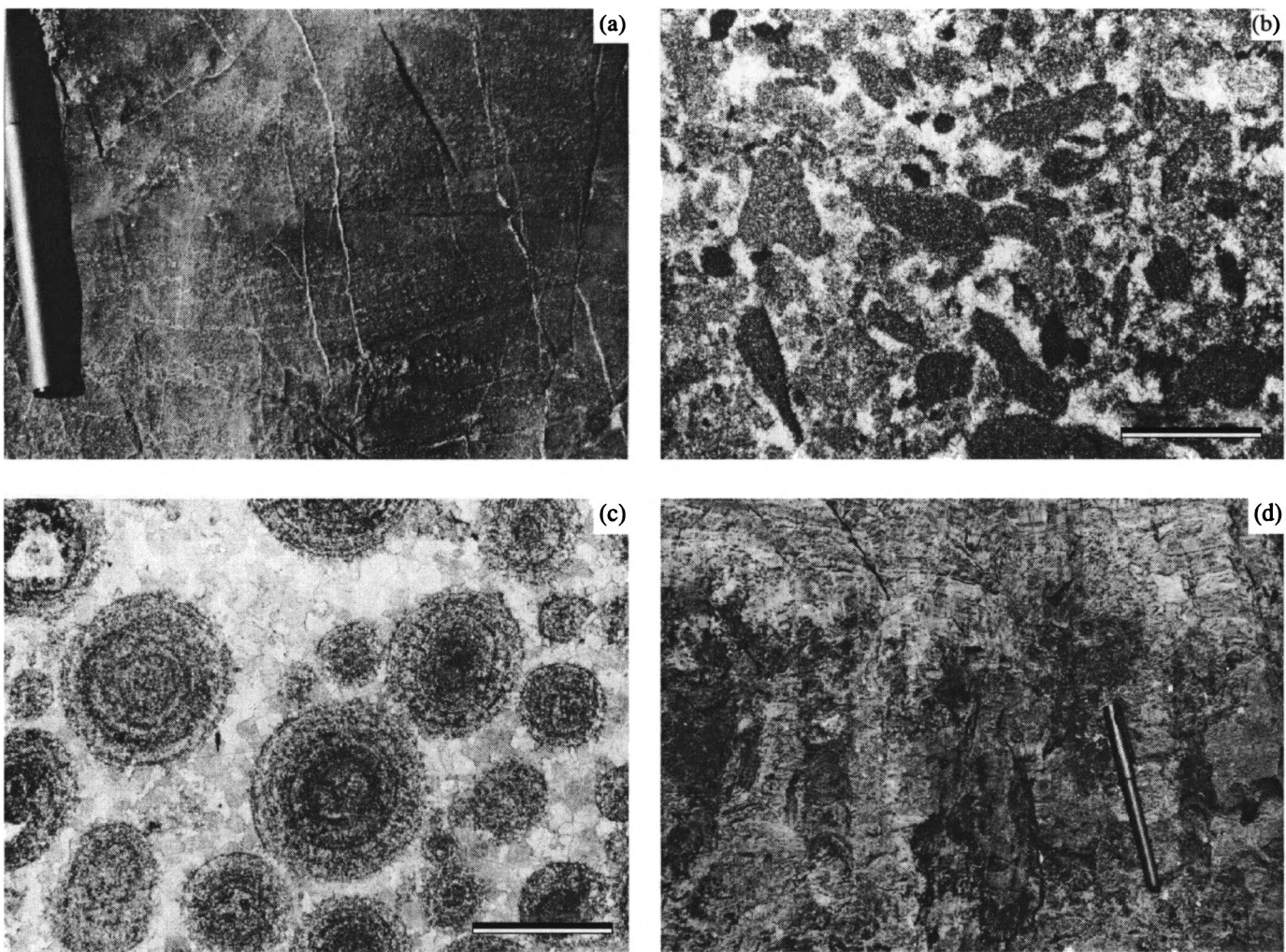


Fig. 4. Cross-stratified grainstone subfacies. (a) Tabular cross-stratification in peloidal grainstone. Pen for scale; (b) photomicrograph of peloidal grainstone. Scale bar 1 mm; (c) photomicrograph of ooidal grainstone. Scale bar 1 mm; (d) thrombolites. Pen for scale.

ric. Polished slabs and thin sections show that the grain sizes range from silt to coarse sand. Larger intraclasts (1–2 cm or bigger) and interbeds of intraformational conglomerates are present in some of the grainstone beds (see below). Most of the grains composing the framework of the grainstone appear to have been initially composed of peloidal mud (Fig. 4b). Although the individual peloids are now replaced by micritic dolomite, their “ghosts” are in many cases visible in thin sections and in the polished slabs. Ooid grainstones (Fig. 4c) are present in one or two beds in the Kok-Soo Section. The ooid grainstone framework is typically composed of individual ooids (up to about 2 mm in diameter) and clasts of early-cemented ooid grainstones (up to 1 cm); pore space within the framework is filled with dolomite cement.

The most obvious depositional structures in the cross-stratified grainstone subfacies include small- and large-scale tabular cross-stratification, climbing (ripple-drift) cross-stratification, small-scale wave-ripple cross-stratification, and hummocky cross-stratification. Also common are intraformational flat-pebble conglomerates, mudstone drapes, grainstones with traces of bioturbation, and structureless grainstones.

Small- to large-scale tabular cross-stratification (Fig. 4a) is the most common structure. Sets of the cross-strata are typically 2 to 10 cm thick with a strong mode around 5 cm. Sets are separated by planar or slightly undulatory bounding surfaces. In some cases, set boundaries are slightly inclined to each other and form gentle wedges. Within the sets, the internal millimeter-scale laminae make a 10° to 30° angle with the set boundaries. In most cases, the contact the foresets make with the lower set boundary is wedge-shaped; however, in a very few cases, internal foresets are tangential to the lower set boundary, producing a trough cross-stratification subunit. Some of the sets display apparent opposite foreset dip directions (“herring-bone” cross-stratification). However, the outcrops never allowed observation of this feature in three dimensions, so that positive identification of the “herring-bone” structure could not be made.

In some cases, the bedforms that produced cross-stratification are preserved in cross-section and are clearly of the current ripple type produced by unidirectional flow. These bedforms are typically about 5 cm high, with steep (20°–30°) foreslope and gentle (less than 10°) backslope, and so fall into the lower range of the 2-D megaripple group (Harms *et al.*, 1982; Middleton and Southard, 1984).

Large amounts of gravel-size material are common in some of the sets. Intraclasts range in size from coarse sand to fine gravel a few centimeters in diameter and typically have discoid shapes (flat-pebbles). Intraclasts are usually positioned along the foresets and at the foreset bases; the long axis of the clasts are parallel or close to parallel to the foreslope dip. The internal textures of

the intraclasts range from grainstone to mudstone (see below).

Another noteworthy feature common in some of the cross-stratified grainstone beds is flattened to spherical intergranular voids a few millimeters in diameter, filled with sediment or, more commonly, with spar. They are especially abundant within the layers containing flat-pebble conglomerates, and are *shelter pores* similar to the *subtidal fenestral-like voids* described by Shinn (1983). Although from a distance, and especially on weathered surfaces, they give the impression of true fenestrae, these pores are really supported by intraclasts of early-cemented grainstones and mudstones, “sheltering” internal space which is generally considerably larger than the size of “regular” pores in such rock. This can be easily seen in the polished slabs and acetate peels.

Another common and very significant feature of cross-stratified grainstones is the draping of grainstone bedforms and layers by mud. In cases where ripples are preserved, mud drapes clearly thin over the tops of the ripples and thicken over their flanks, forming a flat or almost flat upper surface. If the bedforms are not very well pronounced, then mudstone may cover a set of cross-stratified grainstone in a sheetlike fashion. It is also not uncommon to see upwards gradation from cross-stratified grainstone to flat- or undulatory-layered, or even structureless, mudstone in some of the sets. The upper boundaries of the mudstone drapes with the next cross-stratified grainstone set are sharp, and, in some cases, erosional (Fig. 5a).

Hummocky cross-stratification is also common in the cross-stratified grainstone subfacies. Hummocky cross-stratified grainstones may appear in isolated portions of the section or in close interlayering with sets of tabular and trough cross-stratified grainstones. Hummocky cross-stratification is represented by long sets up to few centimeters thick and few tens of centimeters to several meters long. The bottoms of the sets are generally flat or almost flat; the top surfaces very gently convex upward. Internal lamination is present within many sets. In the lowermost parts of the sets, the lamination is parallel to the lower set boundaries. Higher up in the set, the thickness of an individual laminae slightly varies laterally. Resulting dips are never more than a few degrees, and there typically is no preferred dip direction. The hummocky cross-stratified grainstones are characteristically finer-grained than tabular and trough cross-stratified grainstones.

It should be noted that for a positive identification of the hummocky cross-stratification, a three-dimensional outcrop is required. Such outcrops were unavailable in the field, so the exact character of the hummocky cross-stratification could not have been confirmed.

Climbing (ripple-drift) cross-stratification is another significant, though not very widely represented, structure in the cross-stratified grainstone subfacies of the subtidal deposits of Aisha-Bibi. This small-scale cross-stratification has sets usually not

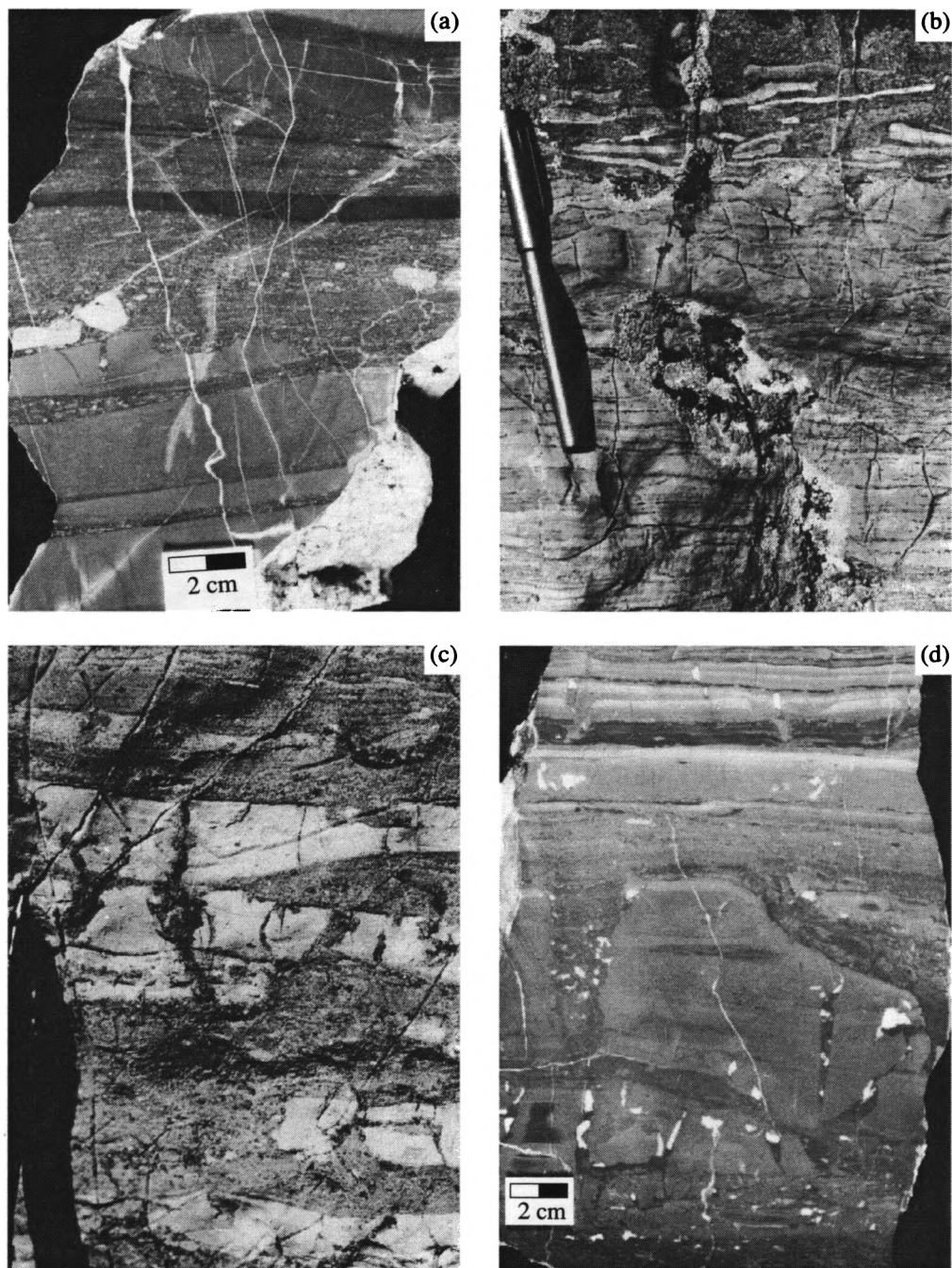


Fig. 5. (a) Cross-stratified grainstone subfacies, Storm-depositional beds. Note gradational boundaries between cross-stratified grainstone units and overlying mud drapes, sharp erosional upper boundaries of mudstones, and intraformational conglomerates; (b) basal flat-pebble conglomerates at the lower cycle boundary. Pen for scale; “ribbon rock” subfacies: (c) sand waves draped by mud (pen for scale) and (d) deep mudcracks in the mudstone interbeds.

thicker than 3 cm. Internal mm-scale lamination is well-pronounced. The height of a ripple is normally about 1 cm and the length is about 5 cm. Some of the boundaries between the sets are inclined; a few of them are erosive, and truncation of the internal lamination can be observed. In most cases, however, the angle of climb is steeper than the slopes of the ripple; thus, laminae are pre-

served at the stoss-side as well as at the lee-side. In some cases, the angle of climb almost reaches 90° (“in-phase” ripples).

Small-scale wave-ripple cross-stratification is rather uncommon in the cross-stratified grainstone subfacies. Wave ripples are small (less than 1 cm high, 1 to 5 cm long) and can be recognized by their symmetrical

cross-sectional shapes, typically with rounded crests. Chevron internal structures, characteristic of wave-ripple cross-stratification, are common at the ripple crests.

Intraformational flat-pebble conglomerates are interbedded with grainstones. They occur as layers and lenses a few centimeters to tens of centimeters thick. Individual clasts also appear randomly throughout the grainstone bed (Fig. 5a). Unlike the basal flat-pebble conglomerates, beds and lenses of these intraformational conglomerates are not concentrated at any particular level within a cycle. Internally, the intraformational conglomerates are poorly sorted, with clast sizes ranging from coarse sand up to gravel size. Most commonly, clasts are 1 to 3 cm long. Clasts typically have discoidal shapes; their thickness is rarely more than 1 cm. Some of the intraformational conglomerate beds have clast-supported fabric, whereas others are sand-supported. These two fabrics grade into each other. Moreover, boundaries between beds and lenses of intraformational conglomerates and overlying and underlying cross-stratified grainstones are also commonly gradational. Most of the intraformational conglomerates show a very crude horizontal layering (most of the elongated clasts are oriented parallel or close to parallel to the general bedding direction). In some beds, there are hints of intraclast imbrication. Intraclast internal textures are varied, ranging from structureless or laminated mudstones to cross-stratified grainstones to structureless grainstones. In general, every type of pebble texture can be correlated to a rock type that occurs within the cross-stratified grainstone subfacies.

Another common feature closely associated with the flat-pebble conglomerates is *soft-sediment deformation* in grainstone beds and draping mudstone layers. Soft-sediment deformation features are especially common in the Aktoogai Section. The deformation takes the form of bent and broken beds overlain and underlain by normal undeformed layering. Beds can be deformed in numerous ways, ranging from gentle synclinal to anticlinal folds, in which case the continuity of the bed has not been compromised, to severe folding that in many cases culminates in beds broken in one or more places. Folding is typically asymmetric and in many instances overturned. However, the dip directions of the axial planes varies from one deformed layer to another and in some cases even within one layer. Commonly the deformed beds are surrounded by flat-pebble intraclasts, evidently separated from the deformed layer.

Significant portions of the cross-stratified grainstone subfacies are composed of *bioturbated or structureless grainstones*. Bioturbated grainstones are mottled with networks of tubes, typically a few millimeters in diameter and a few centimeters long. The tubes do not appear to have a preferential orientation; they are filled either with mudstone, which in most cases also has a slightly different color than that of the host grainstone, or, less commonly, with spar. There is a complete

gradation from cross-stratified grainstone with only a few traces of bioturbation to a completely homogenous and structureless peloidal grainstone-mudstone with no original layering preserved.

Thrombolites (Fig. 4d) have been found only in the Ooshbas Section, and even there they are quite rare (they are present only in three cycles around the 175 m mark). Thrombolites are generally defined as fixed bodies of microbial origin displaying characteristic clotted fabric (Aitken, 1967; Kennard and James, 1986). Thrombolites are common in Lower Paleozoic carbonate deposits and have been described by a number of authors (Aitken, 1967; James and Kobluk, 1978; Kennard and James, 1986; Nguyen, 1986; and others).

Thrombolites occur as relatively small bodies (0.3 to 1.35 m high, up to 10 m wide) composed of vertical "fingers" or small mounds 1 to 30 cm across, extending from the bottom to the top of the body, with sediment-filled interstices between the fingers. Mounds have smooth to irregular sides and generally convex tops. Internally, the fingers display two main structures: (a) stromatolite-like lamination—a finger consists of vertically stacked hemispheroids of thinly interlayered peloidal grainstone and mudstone; the flanks of the hemispheroids are steep and exceed the angle of repose, and (b) random-clotted fabric consisting of clusters of mud outlined and encrusted by films of *Renalcis*-like forms. These two fabrics commonly displace each other vertically and laterally within one finger; clotted fabric is normally (but not necessarily) more common in the upper parts of the finger, whereas stromatolitic fabric is typical for the lower parts.

Interstices, or pockets, between the fingers are a few centimeters to tens of centimeters wide and commonly extend vertically for the entire thickness of the thrombolite. The interstices are filled with cross-stratified grainstones with intraclasts, identical or very similar to those described above. The centimeter-scale interlayering of cross-stratified grainstones and mudstones is also quite common in the uppermost parts of the pockets. Generally, the amount of mud in the infill sediment between the "fingers" increases towards the top of the layer.

Interpretation

The bulk of the grainstones are composed internally of pelleted mud. This indicates that the primary carbonate mud sediment had been turned into sand as a result of reworking, probably by bioturbating organisms. The lack of fossils suggests that most of the bioturbators were probably either soft-bodied or poorly calcified. Such a reworking is very common in the modern shallow-water carbonate depositional environments (see, for example, Garrett, 1977).

In most of the cross-stratified grainstone subfacies, the dominance of sand and gravel and the generally small amounts of mud indicate deposition in a high-

energy environment. Ooid layers are especially mud-free, suggesting that they were probably deposited in an even more hydrodynamically active environment than the rest of the grainstone subfacies. The abundance of intraformational conglomerates (and soft-sediment deformation, see below) indicates at least an occasional very high-velocity water flow. It also indicates the development of early cementation and formation of hardgrounds, especially in the mudstone drapes and sheets. In order for a sediment layer to break as clasts instead of just being redeposited, the sediment has to be at least partially solidified; also, it has to happen quite soon after the deposition. The fact that mudstone intraclasts are generally more common within the intraformational conglomerates than intraclasts composed of grainstone suggests that mud drapes and sheets underwent preferential early cementation.

The dominance of asymmetric ripples and tabular cross-stratification shows that transport and deposition of sand by unidirectional currents was the most important depositional mechanism. Although the outcrop did not allow observation of plan-view shapes of bedforms on the layering surfaces, the fact that tabular cross-stratification is much more common than trough cross-stratification allows us to deduce that most of the sediment migrated in straight-crested (so-called two-dimensional), current-dominated ripples. It also indicates that most of the cross-stratified grainstones were deposited under modest flow velocities, probably in the order of 0.3 to 0.6 m/s if the water depth was at least a few tens of centimeters (see diagrams in Harms *et al.*, 1982; Figs. 2-4, 2-5, 2-6, 2-8). Sediment transport under these conditions must have been mostly in the form of bed load. Discontinuous three-dimensional ripples, which formed trough cross-stratification, are indicative of occasional higher flow velocities. Hints of herring-bone cross-stratification suggest the periodically reversing directions of currents. The most obvious candidate for such currents are tidal currents. Small symmetric vortex wave ripples were also found. This indicates that low to moderate wave activity also played a role in the distribution and deposition of sediment, and also that the depth at which deposition occurred was shallower than wave base. Mechanisms for producing hummocky cross-stratification are still poorly understood; most researchers interpret hummocky cross-stratification as deposits of combined oscillatory-unidirectional flows generated by storms.

Sets of cross-stratified grainstone topped by mud drapes and sheets are also very significant for interpretation of depositional processes and they indicate storm deposition. Typical storm-depositional sequences consist of a planar-laminated and cross-stratified sand unit, commonly with an erosional base covered by mud drapes and sheets. Such sequences are well-known and described both in the modern and ancient deposits (see, for example, Allen, 1984). Sand units in such sequences record deposition under high-energy conditions during the storm, and mud drapes indicate settle-

ment of mud under still-water conditions following the storm. The repetitious character of this sequence (cross-stratified grainstone set → thin mud drape) in Aisha-Bibi deposits suggests that storms could be one of the principal mechanisms responsible for deposition of the sediments composing the cross-stratified grainstone subfacies.

The origin of soft-sediment deformation processes in the cross-stratified grainstone subfacies is not yet entirely understood. Several processes could be responsible for the formation of the described structures. Convolute folding (Allen, 1984; Demicco and Hardie, 1994; Pettijohn and Potter, 1964) is one of the possibilities. Such folding could occur as a result of partial liquefaction of sandy sediment overlying muddy sediment, i.e., gravitational instability due to density differences (Allen, 1984). Such changes in rheology of sediment could be due to a variety of reasons, for example, earthquake tremors. However, the described structures lack several key features of convolute lamination, such as lateral extensiveness and regularity of the folds, their domal or cylindrical shape. Moreover, they display asymmetry, which is highly unusual for convolute folding. Gravitational microslumps (sheet slumps, according to Allen, 1984), resulting from downslope movement of sediment, could also be responsible for the formation of the described structures. Although sheet slumps can form on slopes as low as 0.5°, dip directions of the fold axis should be consistent from one deformed layer to another. This, however, is not the case. Although most of the observed folding is asymmetrical, the asymmetry is irregular and there are no preferred dip directions. Evidence suggests that in this case, the soft-sediment deformation structures have most likely been produced by rip-up of semi-solidified hardgrounds by unusually large (storm) waves.

The tubular structures observed in the grainstones are most likely the burrows of soft-bodied infauna, such as polychaete worms (see extensive description of modern burrows in the Andros Island, Bahamas, tidal flat sediments in Garrett, 1977). Such an interpretation implies that reworking of sediment by organisms occurred in the depositional setting. However, the fact that mechanical depositional structures are largely preserved indicates that mechanical reworking by tidal and storm currents occurred at greater rates than bioturbation.

Thrombolites are usually interpreted as rigid frame-stones, that is, reef bioherms. This interpretation seems to be valid in this case. Indeed, there is little doubt that the origin of Ooshbas thrombolites was microbially influenced. One clear indication of this is the stromatolitic fabric of portions of the thrombolite mounds, especially the fact that the sides of the stromatolite-like domes are steeper than the angle of repose, which is impossible without microbial agglutination.

The thrombolites are underlain and surrounded by cross-stratified grainstones and flat-pebble conglomerates of subtidal lagoonal or shoal origin, which indi-

cates that the thrombolites formed in subtidal conditions. Moreover, the thrombolites seem to reflect in their internal structure the general shallowing-upwards makeup of the cycles: as the amount of sand decreases and the amount of mud increases upwards (from grainstones to "ribbon rocks"), the internal fabric of the thrombolitic "fingers" tend to change from stromatolite-like lamination to random-clotted mud clusters.

These observations suggest that the Ooshbas thrombolites occurred as patch reefs in shallow subtidal shelf environments on the Aisha-Bibi platform. Modern analogs of Aisha-Bibi thrombolites are the patch reefs of Belize (Wallace and Schaferman, 1977). Other, and even closer, analogues are the subtidal stromatolites of the Bahamas (Browne, 1994; Dill, 1991; Dill *et al.*, 1989, 1986; Dravis, 1983; Shapiro *et al.*, 1990). These subtidal stromatolites form in a high-energy environment on modern ooid shoals and are internally partially laminated and partially homogenous.

Based on this analysis of sedimentary structures and the likely depositional mechanisms that generated them, the rocks composing the cross-stratified grainstone subfacies are interpreted to have been deposited in shallow subtidal peloid-ooid sand shoal environment on the carbonate shelf. The cross-stratified sands themselves were transported and deposited by storms and tidal currents as migrating bedforms. Intraformational conglomerates, as well as soft-sediment deformation structures, resulted from the storm rip-up of hardgrounds (storm lag deposits). Mottled and structureless grainstones and mudstones were formed by bioturbation by soft-bodied organisms, such as polychaete worms. Thrombolites represent subtidal patch reefs. The most obvious modern analogues for such a depositional environment are the peloid and ooid shoals of the Bahamas and South Florida (see, for example, Bathurst, 1975; Scholle *et al.*, 1983; and others).

"RIBBON ROCK" SUBFACIES

Description

"Ribbon rock" is an informal field term that has been used for many years by Appalachian sedimentologists to describe thin-bedded peloidal calcitic grainstones interlayered with dolomitic mudstones in the Upper Cambrian Conococheague Formation, Central Appalachians (see Demicco, 1983). In this paper, this term is used to describe the cm-scale heterolithic interlayering of grainstone and mudstone especially common in the Ooshbas and Kok-Soo sections, which bears a striking resemblance to the "ribbon rocks" of the Conococheague Limestone. It should be noted, however, that unlike the Conococheague ribbon rocks, those of the Ooshbas and Kok-Soo sections are presently composed entirely of dolomite.

Grainstone interbeds occur as continuous layers or as lenses (Figs. 5c, 5d). Layers and lenses range in thickness from 5 mm to 10 cm, most commonly being

1–5 cm thick. Layers are laterally continuous on the outcrop scale (a few tens of meters), and lenses can be as small as 5 cm laterally. It is not uncommon for isolated lenses to be laterally connected by grainstone laminae. Grainstone interbeds typically have sharp lower boundaries, commonly with scour marks. Upper boundaries of the interbeds are commonly gradational with grainstones grading up to mudstone interlayers (see below). Symmetric ripple-form tops are common for grainstone layers and lenses.

Internally, the grainstone interbeds have a grain-supported fabric. The grains come in a range of sizes from silt to coarse sand. Individual larger clasts (some as big as 1–2 cm across) are present in some of the grainstone interbeds. Most of the grains appear to have been initially composed of muddy peloids; ooids have not been found. Individual peloids are easily observed on the weathered surface, in polished slabs, and in thin sections.

Internally, grainstone interbeds are either structureless or laminated. Common lamination styles include (a) gradation from coarser-grained sand at the bottom of the interlayer to fine sand and silt at top, (b) low-angle small-scale current-ripple cross-lamination, and (c) symmetrical wave-ripples. The lamination is mainly defined by the differences in grain size.

Mudstone interbeds usually occur as layers a few mm to 10 cm thick that are continuous on the outcrop scale. Some of the mudstone interbeds are clearly draping the wavy upper surfaces of the underlying grainstone layers: they are thicker at the flanks of the grainstone waves and thinner over the crests (Fig. 5c). The lower boundaries of the mudstone interlayers may be either sharp or gradational. Upper boundaries of the mudstone layers are almost always sharp, commonly erosional, with deep scour marks on the surface. It is not uncommon to find intraclasts made of mudstone in the grainstones just above the grainstone-mudstone boundary. This suggests that mudstone layers were quite cohesive soon after their deposition (before the next grainstone interbed was deposited).

Relatively few mudstone layers have traces of internal lamination. Where present, lamination is usually defined by changes in color or the presence of various amounts of sand-sized grains. These grainstone laminae within mudstone interbeds are generally flat, or in some cases slightly undulatory.

Some of the mudstone interbeds have traces of tubular burrows in them. These burrows originate at the upper surfaces of the interbeds, have a tubular shape and are usually quite shallow; it is uncommon to see them penetrate into the underlying grainstones. Many of the tubes are filled with the same grainstone that overlies the particular mudstone interlayer.

One of the most spectacular features in the mudstone interbeds in the ribbon rocks is mudcracks (Fig. 5d). Although most of the mudcracks are quite small (a few mm wide and 1–3 cm deep), some of them can be as

wide as 3–5 cm and may cut through the full thickness of the mudstone interbed (up to 10 cm), and in some cases, even through an underlying layer of peloidal grainstone (especially if the latter is rather thin) down into the next mudstone layer. Most commonly, the mudcracks are V-shaped, although some of the narrower ones have almost parallel walls. Many of the narrower mudcracks in the mudstones are pygmatically folded (cf. molar-tooth structure), showing the effects of vertical compaction of host sediment (mud) around more competent crack filling (Allen, 1984; Demicco and Hardie, 1994). Mudcracks are commonly filled with grainstone, i.e., material identical to the overlying interbed. In some cases, it is possible to observe mud-crack polygons on the bedding surfaces of the mudstone interlayers.

In addition to mudcracks, some of the thicker mudstone interbeds display centimeter-scale soft-sediment deformation features in the form of convolute folding. These deformation features are mostly concentrated in the uppermost parts of the mudstone interlayers on the boundaries between the mudstone and overlying grainstones. The most common morphology for these soft-sediment deformation features is vertically oriented bulges, sacks, and irregular protuberances. These characteristics suggest that the convolute folding resulted from liquefaction of lighter sediment (mud) under the weight of the denser layer (sand) (Allen, 1984; and others).

Disrupted "ribbon rocks" are also very common in the Ooshbas and Kok-Soo sections. This term is used in this paper to describe the subfacies very similar to ribbon rocks, except that the mudstone interlayers are not typically continuous; rather, they either end abruptly or are represented by trains of large (centimeter to tens of centimeters in length) intraclasts. Most of the intraclasts lie either flat or at a low angle relative to the general bedding plane; a few of the smaller ones, however, can be positioned almost edgewise. These discontinuous layers and intraclasts carry in them most of the internal sedimentary features of the "normal" mudstone interbeds, such as thin layers of grainstones, small mudcracks, burrows, etc. The "matrix" in which the disrupted mudstone interlayers are embedded is composed of (peloidal?) grainstones very similar in appearance to those of the grainstone interlayers of the regular ribbon rocks. The same structures that are characteristic of the ribbon rocks grainstones, such as gradational lamination, low-angle current-ripple cross-lamination and symmetrical wave ripples, are also typical for the grainstones of the disrupted ribbon rocks.

Within the cycles, disrupted ribbon rocks always occupy the position directly below the ribbon rocks (and above the subtidal grainstones) and represent the gradual transition from the latter to the former. This transition is usually very smooth, and so it is not always easy to locate the exact lower boundary of the ribbon rock unit.

Interpretation

The origin of ribbon rocks, their depositional environment, and modern analogs have been described in detail by Demicco (1981, 1983) for the ribbon rocks of Upper Cambrian Conococheague Limestone, Central Appalachians, United States. In short, the grainstone–mudstone interlayering reflects original sand–mud deposition alternations on high-tide range, mixed sand–mud intertidal flats like those of the modern North Sea (Reineck, 1960; Reineck and Singh, 1980). In case of the ribbon rocks of the Aisha-Bibi, the rippled and cross-laminated grainstones were deposited by traction by waves or tidal currents. Small-scale ripple cross-lamination, typical for most grainstone interbeds, is characteristic for relatively small water depths and low to moderate flow velocity. The mudstones, however, have features (such as draping morphology over the grainstone ripples) that suggest that mud settled out during the intervening quiet water conditions. This pattern, reflecting deposition by two processes (relatively high-energy deposition of carbonate sand alternating with mud settle-out under low-energy, waning currents conditions) is characteristic for many modern intertidal deposits (see, for example, Reineck, 1960 or Reineck and Singh, 1980). Another important piece of evidence is a clear pattern upsection from disrupted ribbon rocks to ribbon rocks with continuous mudstone interlayers (thin in comparison to adjacent grainstone interlayers) to intensely mudcracked ribbon rocks with relatively thick mudstone interbeds and relatively thin grainstones. This pattern is observed in most cycles and reflects shallowing-upward conditions within the ribbon rocks subfacies. Mudcracks in the uppermost ribbon rocks of individual cycles imply that the deposition of mudstone interbeds has been followed by subaerial exposure. All this evidence suggests that disrupted ribbon rocks and possibly the lowermost parts of normal ribbon rocks were deposited in the shallowest subtidal environment, whereas most of the normal ribbon rocks reflect the progressively shallowing-upwards deposition in intertidal and possibly lowermost supratidal environment (as evidenced by such exposure features as mudcracks and also the fact that the relative amount of grainstone tends to decrease upsection). Although there are no modern carbonate analogs of the ribbon rocks, these deposits, as Demicco (1983) has pointed out, are strikingly similar to sediments deposited in shallow subtidal and intertidal environments on modern siliciclastic tidal flats with a meso- to macro-tidal range (>4 m) (Evans, 1975; Larsonneur, 1975; Reineck, 1960, 1972; Reineck and Singh, 1980).

LAMINITE SUBFACIES

Description

Laminites are very common in all of the described sections and are present at the top of virtually every cycle. Laminites typically have a very sharp, commonly

erosional, upper boundary with the overlying basal flat-pebble conglomerates and cross-stratified grainstones of the next cycle and have a gradational lower boundary with the underlying ribbon rocks, usually so gradational that it is difficult to pinpoint in the field.

Lamination consists of the interlayering of dolomitic grainstone and mudstone on a sub-millimeter to millimeter scale (Figs. 6a, 6c). Boundaries between the individual laminae are generally quite sharp. In a number of cases, however, grainstone laminae clearly grade up to mudstone. Most of the laminae are laterally continuous, and only a few have been observed to pinch out on a meter scale. There are two main styles of lamination that grade into each other: wavy and parallel. In the first case, both top and bottom of the laminae are wavy to the same extent, or, most commonly, the bottoms of the laminae are gently undulatory, whereas the tops display steeper waves. The waves are generally low-amplitude, with wave heights typically on the order of 5 mm and lengths ranging from a few centimeters to tens of centimeters. The waves are composed of grainstone and are covered by mudstone drapes. In some cases, the uniform style of lamination is interrupted by unusually thick (up to a few centimeters) mudstone layers or by uneven grainstone layers or lenses of about the same thickness.

Stromatolites (Fig. 6d) are present in many of the cycles in the Ooshbas and Kok-Soo sections; they are less common and not as well-defined in the Aktoogai Section. They are concentrated in the same layers as laminites and generally are laterally linked to them. As with the laminites, stromatolites are composed of thinly (millimeter-scale) interlayered mudstone and peloidal grainstone, but differ in the arrangement of laminae into vertical stacks of more or less geometrically regular hemispheroids. Most of the stromatolites are fairly small in size (usually on the order of up to a few tens of centimeters in height and width). The stromatolites are typically domal, SH type. The flanks of the stromatolite domes are typically, although not always, quite steep and commonly exceed the angle of repose. Grainstone and mudstone laminae that compose the stromatolites generally tend to be thicker on the flat tops of the domes and in depressions near the bottoms of the flanks and thinner on the steep flanks. Classic LLH stromatolites are rare.

Mudcracks are a common feature within the laminites in the Ooshbas Section; they are rarer in Aktoogai and Kok-Soo cycles. Mudcracks always open into the mudstone laminae; they can also penetrate several underlying couplets of mudstone-grainstone laminae. There are several styles of mudcracks, such as shallow cracks (up to 1 cm deep), wide cracks, deeper irregularly positioned narrow cracks, and prism cracks (Fig. 6a). The latter are deep (up to 10 cm or deeper), approximately equispaced laterally with a typical distance between two neighboring cracks being 10–20 cm, and in many cases clearly multiply filled with internal

layers of mudstone and grainstone. In cross-section, many of the narrow mudcracks have been observed to be pygmatically folded. In a few cases (where allowed by exposure) it could be seen that mudcracks form polygons on the bedding surface (Fig. 6b).

A few of the mudstone laminae, or stacks of a few laminae, are disrupted, torn apart, deformed and brecciated; this usually occurs locally in individual layers, underlain and overlain by normally layered laminites. Parts of laminated layers up to a few centimeters thick are curled and bent so severely that they are reminiscent of “jelly-roll” structures (Demicco and Hardie, 1994); however, actual “jelly-rolls” have not been detected. Laminite intraclasts are found in some of the brecciated horizons. Intraclasts are generally flat, but in many cases are also slightly bent or curled at the edges, and are typically up to a few centimeters in thickness and in some cases as long as 20 cm. Internal flat-to-wavy lamination is usually well-preserved within these intraclasts.

Interpretation

Several processes can be responsible for producing lamination. The first and most likely possibility is laminite formation by agglutination of sand and mud on microbial (cyanobacterial) mats in shallow subtidal to supratidal zone (Demicco and Hardie, 1994; Ginsburg, 1975; Hardie, 1977; Shinn *et al.*, 1969; and others). Other possibilities include bedload deposition of sand by waves and storm deposits or unidirectional tidal currents alternating with mud settle-out from the suspension. Similar structures can be produced by chemical precipitation with or without microbial influence. Chemical precipitation without microbial influence is known to produce isopachous continuous laminae with thicknesses that do not vary laterally; structures of radial crystal growth are also common in the deposits produced by this mechanism. The Aisha-Bibi laminites, however, are commonly characterized by varying thicknesses of individual laminae and radial growth has not been observed in them. The second mechanism (bedload deposition of sand followed by settle-out of mud) usually requires the presence of mechanically produced bedforms and small-scale cross-stratification. Crinkled lamination is uncommon for this process. This mechanism may have been responsible for deposition of some of the Aisha-Bibi laminites (i.e., the ones with parallel lamination).

As noted previously, there is some evidence of bedload sand deposition (small sand waves) coupled with mud settle-out. However, the other mechanism, namely agglutination of sediment on the surface of microbial mats, seems to be the more plausible one for explaining the origin of most of the Aisha-Bibi laminites. The presence of thin (mm-scale) interlayering of grainstone and mudstone supports the hypothesis of microbially influenced sedimentation: thin couplets of carbonate sand and mud have been observed in numerous modern peritidal cyanobacterial mats. Wavy to crinkled shapes

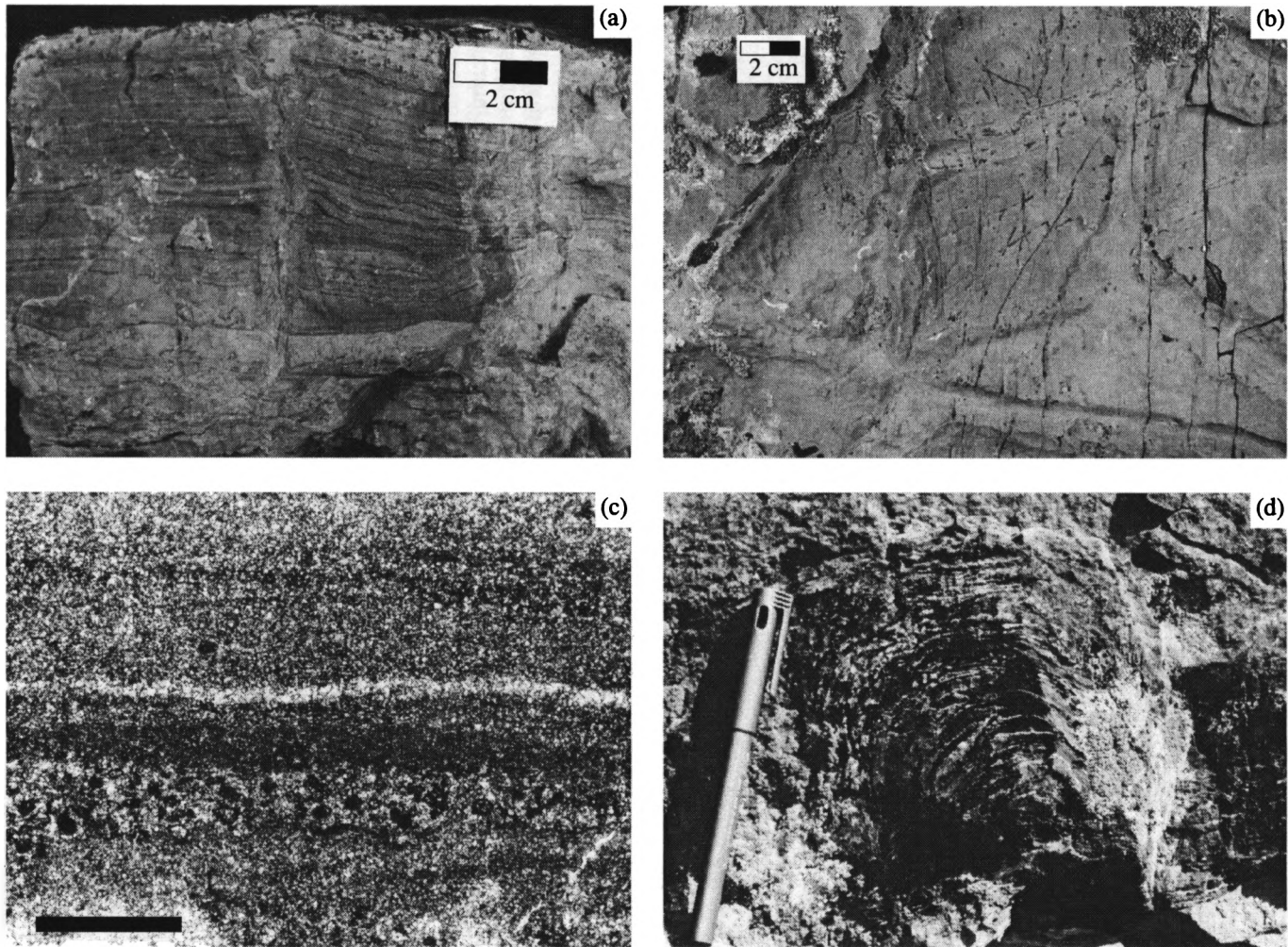


Fig. 6. Laminite subfacies. (a) Mudcracked laminite; (b) top bedding surface of mudcracked laminite. Note characteristic polygonal mudcracks; (c) photomicrograph of laminite. Note interlayering of fine-grained peloidal grainstone and mudstone. Scale bar 2 mm; (d) domal SH stromatolite. Pen for scale.

Subfacies of Aisha-Bibi cycles and their modern analogs

Aisha-Bibi subfacies	Depositional subenvironment	Some modern analogs
Basal flat-pebble conglomerate		Transgressive lag deposits; no direct modern analogues known
Cross-stratified grainstone	Subtidal zone, depth 1–10 m	Subtidal peloid and ooid sand shoals of Bahamas (Ball, 1967, Bathurst, 1975). Thrombolites—patch reefs of Belize (Wallace and Schafersman, 1977) and subtidal stromatolites of Bahamas (Browne, 1994; Dill, 1991; Dill <i>et al.</i> , 1989, 1986; Dravis, 1983; Shapiro <i>et al.</i> , 1990)
“Ribbon rock”	Shallow subtidal and intertidal zone, tidal range 2.6–7 m	Interbedded tidal flat sands and muds of North Sea (van der Berg, 1980, Evans, 1975, Reineck, 1960, 1972, 1975, Reineck and Singh, 1980), English Channel (Larsonneur, 1975), and Georgia Coast, USA (Howard and Frey, 1975)
Laminite	Upper intertidal and supratidal zone	Laminites—tidal flat sediments associated with cyanobacterial mats of Bahamas (Hardie, 1977), Arabian Gulf (Bathurst, 1975, Hardie and Shinn, 1986, Schneider, 1975), Western Australia (Logan <i>et al.</i> , 1974). Stromatolites—intertidal stromatolites of Shark Bay, Western Australia (Davies, 1970, Logan <i>et al.</i> , 1964, 1974) and Florida (Gebelein and Hoffman, 1973)

of individual laminae are also characteristic for microbial mats. The stromatolites of the Aisha-Bibi peritidal cycles also appear to have been formed by agglutination of sediment on microbial mats. First, the stromatolites are built of interlayering of mudstone and peloidal grainstone; the grainstone laminae commonly exceed the angle of repose (“defy gravity”). This is common for microbial stromatolites. Second, lamination within stromatolites is not isopachous (which would be typical for chemically precipitated stromatolite), but, rather, the laminae are commonly thicker on the flat tops of the stromatolite domes and thinner on the steep flanks. Clotted fabrics or carbonate tubules that would indicate chemical precipitation with microbial influence have not been observed. Finally, and most significantly, the stromatolites are typically found in lateral relationship with laminites. This suggests that they were formed by a similar, if not the same, mechanism and in the same environment as the latter.

The deformation of parts of laminite layers also supports the microbial mat hypothesis. The presence of folding, “jelly-roll”-like structures and brecciation supports this interpretation as well. These structures have probably been formed as a result of storms that in modern tidal flats tear microbial mats apart and bend and roll them down-current together with the sediment that is bound to the mat (Demicco and Hardie, 1994; Davies, 1970; Harrison, 1971). In addition, the presence of mudcracks as well as occasional spherical and subspherical fenestrae within the laminites indicates that the sediment surface was exposed for significant periods of time. So, it can be concluded that the Aisha-Bibi laminite subfacies was most likely formed by sediment agglutination on microbial (cyanobacterial) mats and possibly bedload sand deposition coupled with mud settle-out in the upper intertidal to supratidal environment.

RESULTS AND SIGNIFICANCE OF THE STUDY

This study is the first detailed analysis of the subfacies and corresponding depositional environments of the shallow-marine facies of lower Paleozoic Aisha-Bibi seamount. We determined for the first time that the shallow-marine carbonates of the Aisha-Bibi seamount show definite evidence of cyclicity in the form of repeating sequences of peritidal subfacies. In several sections, stacks of tens to more than a hundred cycles occur. Each cycle is composed of a systematic sequence of subfacies from subtidal at bottom of the cycle to supratidal at the top. All the subfacies have been thoroughly described and analyzed. As a result, we determined that the principal subfacies composing the Aisha-Bibi cycles can be correlated to corresponding deposits of modern carbonate depositional environments (table). It is easy to see that the sequence of subfacies within each cycle (subtidal grainstones to intertidal ribbon rocks to upper intertidal–supratidal laminites) reflects deposition under shallowing-upward conditions.

This style of deposition seems to be quite a common motive for Lower Paleozoic shallow-marine carbonates around the world (see, for example, Hardie and Shinn, 1986 or Demicco and Hardie, 1994). The Cambrian–Ordovician deposits of the Appalachians in the United States are especially well known. Examination of these deposits shows that the subfacies involved are strikingly similar to those of shallow-marine carbonates of Aisha-Bibi. Depositional cycles in the Appalachian deposits are also asymmetrical. The larger scale depositional picture is also quite similar. It is common for the Appalachian Cambrian–Ordovician carbonates to compose stacks of meter-scale shallowing-upward cycles.

Although it is clear that stacks of shallowing-upward cycles represent episodic relative sea level

changes, the exact nature and origin of these oscillations remain unclear and controversial (see, for example, Koerschner and Read, 1989 and Hardie *et al.* 1991). There are several hypotheses that attempt to provide an explanation for the origin of such high-frequency sea level changes and suggest mechanisms capable of producing stacks of shallowing-upward cycles. These mechanisms include autocycles (Ginsburg, 1971), nonuniform platform subsidence, tectonic pulses, and, finally, periodic eustatic sea level oscillations in tune to Milankovitch orbital changes (Berger *et al.*, 1984; Schwarzscher, 1993; and others).

Research effort currently underway at Johns Hopkins is aimed at tackling the problem of origin of high-frequency depositional cycles in shallow-marine carbonates using advanced time series analysis, two-dimensional computer modeling of carbonate platform deposition and the resulting facies geometry, and comparative studies of cyclic shallow-marine carbonates around the globe. Preliminary results of this research indicate that the origin of cyclicity in the shallow-marine carbonates of Lower Paleozoic Aisha-Bibi platform has been strongly influenced by orbital forcing (Bazykin and Hinnov, 1996).

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Paleogeography of Burzyan in Stratotypical Locality

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Abstract—The structure of Lower Riphean deposits of the Bashkirian Meganticlinorium in the southern Ural, the correlation of sections, and the deposition conditions are discussed. The examination of sedimentation systems and main trends in distribution of sedimentary complexes of various composition and origin made it possible to elaborate a new set of schemes of lateral relationships for all lithostratigraphic subdivisions of the Burzyan stratotype. The analysis of available data does not confirm recent concepts concerning the local linear riftogenic nature of volcanogenic sedimentary rocks at basal levels of Lower Riphean. On the contrary, paleogeographic reconstructions indicate that during the Early Riphean the territory under consideration was a part of rather large epiplatform sedimentation basin.

The reconstructions of environments, in which Riphean sedimentary associations were formed, still occupy a modest position in the Russian literature concerning Upper Precambrian. Above all else, it is caused by an insufficiently detailed typification of sediments, a conventional character of correlation between most lithostratigraphic subdivisions in context of regional correlation schemes, a lack of reliable criteria determining the limits of aforesaid subdivisions in different zones of sedimentary basins, convergent geochemical indicators of sedimentation, etc. For a long time, the attention of Russian researchers was attracted to the elaboration of lithostratigraphic scales for different regions, whereas in foreign literature a distinct, solely sedimentological approach prevailed; only in recent years the progress in this approach has reached our country (Petrov, 1993a, b; Tanygin, 1992; Veis and Petrov, 1994). The elucidation of paleogeography related to certain sedimentation basins is a cornerstone of general models describing the sedimentogenesis and evolution of both Phanerozoic and ancient (Riphean, and pre-Riphean) sedimentary basins (Timofeev, 1992).

This paper is devoted to the characteristics of main lateral relationships between Early Riphean sedimentary complexes at the present-day western slope of the southern Ural. The work is based on the results of lithostratigraphic studies (Maslov and Krupenin, 1991, and others) and the detailed lithofacies analysis of Burzyan deposits in the Bashkirian Meganticlinorium (Kozlov *et al.*, 1989; Maslov, 1991, 1993; Maslov and Kuleshova, 1988). It should especially be stressed that according to the current knowledge, Riphean sedimentary successions in the western part of the southern Ural were formed within a large sedimentation basin that once covered a vast area from Samara to Zlatoust (?), from Orenburg to Perm and probably further to the north (Maslov *et al.*, 1994).

The typical Burzyan section is represented by complexes of various composition and origin, among which both intrabasin and continental “near-border” or “border” sediments can be recognized. Detailed reconstructions of its evolution based on lithofacies maps at a scale of 1 : 500000 are now available for most lithostratigraphic levels of the Burzyan Group at the southeastern flank of this sedimentation basin covering the stratotypical locality of Riphean.

The comprehensive analysis of current concepts concerning the accumulation conditions for Lower Riphean sedimentary successions in the Bashkirian Meganticlinorium was reported previously; the review and bibliography see in (Maslov, 1993, 1994). At least two alternative viewpoints in interpretation of the sediment genesis and paleogeography of Early Riphean at the western slope of the southern Ural exist. Some authors considered and still consider Early Riphean deposits typical marine miogeosynclinal sediments and assume a possibility of continental sedimentation only for Early Burzyan deposits (Anfimov, 1982; Anfimov *et al.*, 1983; Bekker, 1988; Garan', 1946, 1963; *Geologiya ...*, 1977; Keller *et al.*, 1968; Olli, 1948; Shvetsov, 1974; Yakobson, 1968; Yakobson and Kazak, 1978). Other researchers consider the same deposits from the standpoint of “riftogenic depression hypothesis” (Ablizin *et al.*, 1982; Ivanov, 1980; Kurbatskaya, 1985; Parnachev, 1982, 1986, 1987b). For example, as Parnachev and coauthors (1982) wrote, *the coexistence of subaerial trachybasalts and continental coarse-grained molasse-related rocks in the Ai Formation indicates that the accumulation of sedimentary complexes of that time occurred under conditions of graben-like structure*. In subsequent works the sedimentation basins of Satka and Bakal times are considered as marine or intracontinental lacustrine depressions with a relatively rugged bottom relief. Specific features of these basins presumably included the significant migra-

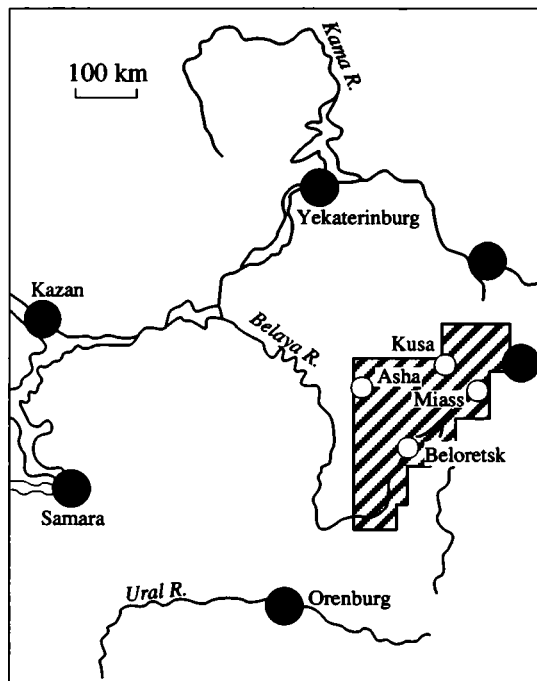


Fig. 1. Territory of the studied western slope of the southern Ural, the Bashkirian Meganticlinorium.

given in order to clarify general features of the Burzyan paleogeography in stratotypical locality discussed below.

The Ai Formation is composed of diverse terrigenous, volcanogenic, and volcanogenic sedimentary rocks. In the submeridional segment of the Ai River system northwest of Zlatoust it was subdivided by M.I. Garan' (1963, 1969) into four subformations: Lipov, Chudinka, Kiseگان, and Sungur. The Lipov subformation consists of arkose sandstones with siltstone and gritstone interlayers. The Chudinka subformation comprises shales, siltstones, sandstones, and conglomerates. Kiseگان and Sungur subformations are almost entirely represented by carbonaceous shales. As was established by V.I. Petrov and coworkers from the large-scale surveying (Lennykh and Petrov, 1974, 1978), in the framework of the Taratash Massif northeast of Kusa town, the lower part of the Ai Formation is composed of terrigenous rocks and trachybasalts (Navysh subformation) and the upper part—mainly of dark shales and carbonaceous shales with rare siltstone, sandstone, and dolomite interlayers (Efremov subformation). Several versions of correlation between the Ai Formation sections in two aforementioned districts were proposed (Kozlov, 1990; Kozlov *et al.*, 1989; Maslov and Krupenin, 1991; Parnachev *et al.*, 1990). However, the ambiguity of stratigraphic inferences does not hamper the consideration of main features of sedimentary complex distribution in the Ai Formation (see below). In some recent works (Kozlov, 1990; Kozlov *et al.*, 1989) the Efremov subformation is correlated with Chudinka, Kiseگان, and Sungur subformations.

The Satka Formation is composed of carbonate chemogenic (predominant) and phytogenic rocks; shale and carbonaceous shale units, siltstones, marls are of subordinate importance. Garan' (1963, 1969) subdivided the Satka Formation into five subformations (from bottom to top): lower Kusa, upper Kusa, Polovinka, lower Satka, and upper Satka. The lower Kusa subformation is mainly represented by grey and dark grey chemogenic dolomites; phytogenic, clayey, and sandy dolomites, as well as limestones play a subordinate role. The upper Kusa subformation comprises chemogenic grey to dark grey dolomites (predominant), clayey dolomites, and phytogenic carbonate rocks with thin interlayers of shales and carbonaceous shales. The Polovinka subformation mainly consists of carbonaceous shales with rare interlayers of siltstones and carbonate rocks. The lower Satka subformation comprises chemogenic, clayey, and sandy dolomites and subordinate dolomitic marls, carbonaceous shales, shales, phytogenic carbonate rocks. The upper Satka subformation is represented by grey and dark grey dolomites with interlayers of clayey and marly varieties, carbonaceous and carbonate shales, limestones and carbonate breccias with flat fragments. The total thickness of the Satka Formation is about 3300–3500 m (Anfimov *et al.*, 1983).

tion of paleogeographic zones, the clear-cut stromatolite reefs that separated "evaporite reservoirs" from open ocean (!—A.M.) and some other characteristics. As a principal feature related not only to Burzyan, but to the entire typical section of Riphean, Parnachev (1986) pointed out "**the existence of numerous small basins** (my remarks, in bold types) **at different stages of evaporite accumulation within the present-day limits of the Bashkirian Meganticlinorium ... Land sectors that separated the basins could serve as local provenances of clastic material ...**". However, let us try to understand whether it was actually the case.

THE GENERAL CHARACTERISTICS OF BURZYAN SECTIONS IN THE BASHKIRIAN MEGANTICLINORIUM

Lower Riphean deposits of the Burzyan Group in the northeastern Bashkirian Meganticlinorium are known in the framework of the Taratash Anticlinorium and south of it in the central part of the Yamantau Anticlinorium. In the framework of Taratash Anticlinorium they are subdivided into the Ai, Satka, and Bakal formations and in the central part of the uplift are represented by the Bol'shoi Inzer, Suran, and Yusha Formations (Kozlov *et al.*, 1989; *Stratotip...*, 1983) (Fig. 2). The detailed, layer by layer description of Lower Riphean sections, rock textures and structures were reported in (Kozlov *et al.*, 1989; Krupenin, 1986a; Maslov and Krupenin, 1991). In this paper only a brief description of the composition and structure of rock formations are

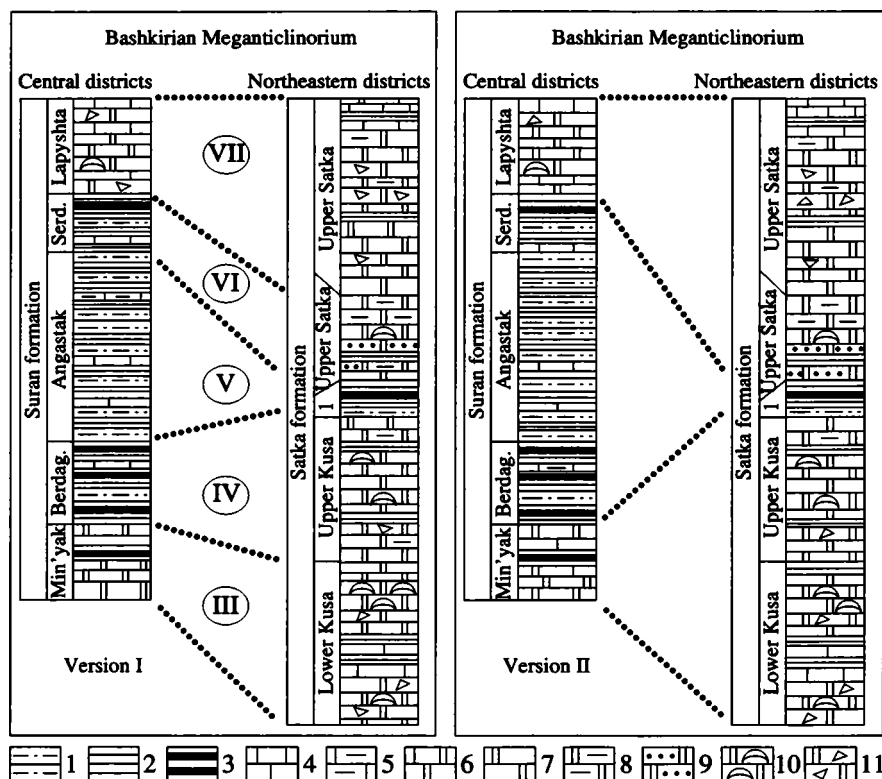


Fig. 2. Versions of correlation between the Satka Formation in the northeastern Bashkirian Meganticlinorium and the Suran Formation in the central part of the meganticlinorium.

(1) siltstones; (2) shales; (3) carbonaceous shales; (4) limestones; (5) clayey limestones; (6) dolomitic limestones; (7) dolomites; (8) clayey dolomites; (9) dolomites with terrigenous sandy-silty admixture; (10) stromatolitic dolomites; (11) dolomites with interlayers of flat-clastic sedimentation breccia.

Roman numerals in circles are selected paleogeographic sections; the number 1 in columns denotes the Polovinka subformation of the Satka Formation.

The Bakal Formation comprises shales and carbonaceous shales, dolomites, calcareous dolomites, limestones and subordinate phytogenic carbonate rocks and siltstones. The total thickness is about 1400–1500 m (Stratotip ..., 1983), approximately 650 m of which fall on the lower (Makarovo) subformation represented mainly by dark-colored carbon-poor shales. The upper (Malobakal) subformation comprises terrigenous and carbonate members and units. The complicated cyclic structure of this stratigraphic level is most evident in sections of the Bakal ore field. To the east and southeast of Bakal the carbonate members are gradually pinched out; the eastern sections are mainly composed of fine-grained sandstones and siltstones intercalating with shales, which are referred to the Korelka unit (Garan', 1963, 1969; Sergeev, 1963; Stratotip ..., 1983).

The Bol'shoi Inzer Formation is mainly represented by fine- and medium-grained sandstones; carbonaceous shales, siltstones, dolomites, and limestones are of subordinate importance. The total thickness of the formation is about 2200 m (Kozlov *et al.*, 1989).

Like the Satka Formation, the Suran Formation is subdivided into five subformations (from bottom to

top): Min'yak, Berdagulovo, Angastak, Serdauk, and Lapysha. The Min'yak subformation comprises dolomites and limestones with thin interlayers of carbonaceous and carbonate shales. The Berdagulovo subformation is mainly represented by ordinary shales along with carbonaceous and carbonate shales. The Angastak subformation consists of fine-grained siltstones, shales, silty shales, dolomites, and their clayey and marly varieties. The Serdauk subformation is represented by units and members of nonuniformly intercalating carbonaceous shales and siltstones; rare clayey and carbonaceous limestones are present. The Lapysha subformation is composed of limestones and dolomites; in some sections the alternating terrigenous and carbonate members are observed as well as interlayers of siltstone, fine-grained sandstone, and carbonate breccia. The thickness of the Suran Formation is estimated as 1000–2800 m (Maslov and Krupenin, 1991).

The section of Lower Riphean in the Yamantau Anticlinorium is terminated by the Yusha Formation composed of shales, carbonaceous shales, siltstones, and less frequent sandstones. Three subformations are recognized: Vyazovo, Bagarysha, and Sukhino, which are mainly distinguished by the shale-to-sandstone

ratio; the sandstones are more frequent in the Bagaryshhta subformation. The thickness of the Yusha Formation ranges from 700 to 1000 m.

SEDIMENTATION SYSTEMS AND SEDIMENTARY COMPLEXES IN THE BURZYAN GROUP

The study of textures and structures of terrigenous and carbonate rocks at the western slope of the southern Ural, the interpretation of facies conditions of sedimentation, the analysis of their spatial relationships and the section structure indicate that a wide spectrum of deposits (may be except most deep-water sediments) are present in the Burzyan Group involving various types of sedimentation systems. Leaving their comprehensive characteristics for a separate paper, we will only define them briefly.

Lower levels of the Ai Formation are composed of terrigenous deposits of the foothill fans (after V.I. Popov) and to a considerably less extent, the well-developed alluvial systems. The deposits from the upper Ai level and from some levels of the Suran Formation are represented by sediments of the outer shelf, which were probably deposited below the wave agitation level. Lower and upper Kusa, as well as the lower and upper Satka levels and their counterparts in central part of the megaanticlinorium are composed of deposits related to the sedimentation systems of carbonate shelf. Lower Bakal sediments resulted from the terrigenous sedimentation in the outer shelf basins below the ordinary wave agitation level in the humid or quasihumid conditions, as follows from the elevated C_{org} content in shales. The deposition of the Malobakal subformation was probably related to the alternating influence of carbonate platform and terrigenous near-shore systems (mixed wave and tidal model, after P. Allen and J. Allen, 1990). These systems were replaced southward and southwestward by the deposits of terrigenous shelf system with predominant wave dispersion of clastic materials (Yusha level). Taking the above interpretation into account, we have delineated a series of large sedimentary complexes of various composition and origin that take part in the Burzyan Group of the typical region. These complexes were formed under specific paleogeographic, paleotectonic, and paleoclimatic (?) conditions.

The reconstruction of lateral relationships between these complexes at different levels of the Burzyan Group revealed the correlation of the aforesaid sedimentation systems and allowed us to clarify the paleogeography and main evolutionary trends for the eastern flank of the Volga-Uralian sedimentation basin in the Early Riphean.

Terrigenous deposits are represented by the following five complexes: mainly continental, polymictic to arkose, volcanogenic terrigenous deposits, terrigenous, arkose and subarkose (alluvial and alluvial-deltaic) deposits; coastal-marine and shallow-marine (feld-

spar-quartz and quartz) deposits; and shallow-marine and marine sediments located far enough from the sources of clastic materials and wave agitation zones. Carbonate complexes include littoral deposits, shallow-marine sediments (frequently with stromatolites and terrigenous admixture), and basin sediments properly removed from onshore zones and provenances.

The genetic interpretation and detailed characteristics of all these complexes were reported previously (Maslov, 1991).

MAIN FEATURES OF SEDIMENTARY COMPLEX DISTRIBUTION IN THE BURZYAN GROUP SECTIONS OF THE SOUTHERN URAL

The above brief description of the Burzyan Group sections provides the stratigraphic framework for the analysis of main trends in the distribution of sedimentary complexes. However, various versions in the interpretation of this framework and, consequently, the compilation of lithofacies maps exist.

It is now generally recognized that "... the Ai, Satka, Bakal formations, on the one hand, and Bol'shoi Inzer, Suran, Yusha formations, on the other hand, represent a common sedimentation cycle ..." (Kozlov *et al.*, 1989), and as was emphasized previously, "... Bol'shoi Inzer, Suran, and Yusha formations are coeval with Ai, Satka, and Bakal Formations, respectively ..." (*Stratotip ...*, 1983).

Except Satka and Suran formations, all formations of the Burzyan Group are divided into an unequal number of lithostratigraphic units (subformations); Satka and Suran formations have similar five-unit structure but are characterized by different composition of subformations. All this hampers the analysis of lateral relationships between sedimentary complexes. Indeed, three subformations are recognized within the Bol'shoi Inzer Formation, and correlation of them with five subformations of the Ai Formation (Kozlov, 1990; Kozlov *et al.*, 1989) is not universally adopted. Problems of correlation of Ai Formation in the Ai River basin and in the framework of Taratash Massif remain unsolved, and this makes all constructions still more difficult (Kozlov *et al.*, 1989; Parnachev *et al.*, 1990). The correlation of subformations in Satka and Suran formations also admits at least two versions (Fig. 3). The first version consists in the direct comparison of subformations in both formations. The second version assumes that thick carbonate successions of lower Kusa, upper Kusa, lower Satka, and upper Satka subformations, on the one hand, and Min'yak and Lapyshka subformations, on the other hand, may be considered as subdivisions with synchronous limits; i.e., the onset and the end of accumulation of these carbonate complexes were nearly contemporaneous all over the Bashkirian Meganticlinorium. The Bakal Formation is divided into two subformations, whereas the Yusha Formation, into three subformations, which are devoid of carbonate rocks;

possible versions of their correlations are numerous and conventional.

Without discussing in detail all problems outlined above, we will focus our attention on those levels of the Burzyan Group that were chosen for the analysis of sedimentary complex distribution. It should be emphasized once again that until now the problems under discussion remain questionable even from the stratigraphic viewpoint; therefore, the statements presented below are to a certain degree a matter of convention.

Sections of the Ai Formation can be naturally subdivided into two parts. The lower part comprises mainly coarse-grained terrigenous rocks of Navysh, Lipovo, and Chudinka subformations. The upper part is mainly represented by shales and carbonaceous shales of Kiseگان and Sungur subformations. The Efremov subformation is correlated only with the upper part of the formation. This determines the choice of two sections for the Ai-Bol'shoi Inzer level. The first section includes the lower part of the Ai Formation and presumably two lower subformations of the Bol'shoi Inzer Formation, which are almost devoid of carbonate rocks. The second section is related to the deposition of upper part of the Ai Formation and, conditionally, to the third subformation of the Bol'shoi Inzer Formation.

As for the Satka-Suran level, it seems unlikely that thick carbonate successions of the Satka Formation are of the same age as relatively thin limestones and dolomites of the Suran Formation in central districts of the meganticlinorium (version II). In both cases shallow-water and basinal carbonate sediments with nearly equal accumulation rates are predominant. Another argument making the first version preferable is the unbalance in thickness variation of the apparently coeval (according to the version II) subformation, i.e., Polovinka subformation, on the one hand, and Berdagulovo, Serdauk, and Angastak subformations, on the other hand. If preference is given to version II, we should find a satisfactory explanation as to why under generally quiescent tectonic regime of the Satka-Suran time, the thickness of terrigenous rocks of this age varies by almost one order of magnitude at a distance less than 150 km. In the case of approximately similar depositional environment for fine-grained terrigenous sediments related to the Satka and Suran formations in both parts of the meganticlinorium, this fact remains unexplained. Keeping this in mind, the subformation limits are assumed to be more or less synchronous, and just version I was used as a basis for the compilation of lithofacies maps and schemes demonstrating the distribution of sedimentary complexes at the Satka-Suran level.

As to the Bakal-Yusha level, the monotonous facies composition of the entire Yusha Formation (represented mainly by basinal, shallow-marine sediments) makes it expedient to accept the contrast model of the Bakal Formation, which consists of two distinct parts, i.e., Makarovo and Malobakal subformations. Hence, one

Bashkirian Meganticlinorium									
Kusa district				Bakal-Satka district				Central districts	
Bakal formation								Yusha formation	Sukhino subformation
									Bagaryshta subformation
Satka formation								Suran formation	Vyazovo subformation
									Lapyshsta subformation
									Serdauk subformation
									Angastak subformation
									Berdagulovo subformation
Ai formation								Bol'shoi Inzer formation	Min'yak subformation
									Upper subformation
									Middle subformation
									Lower subformation

Fig. 3. Lithostratigraphic subdivisions of Lower Riphean of the Bashkirian Meganticlinorium and levels of schematic distribution of sedimentary complexes of various composition and origin (denoted by numerals in circles).

of the paleogeographic sections corresponds to the Makarovo subformation (Bakal Formation) and, by convention, Vyazovo subformation and lower part of Bagaryshta subformations (Yusha Formation). The second section corresponds to the rocks of Malobakal subformation, on the one hand, and Sukhino subformation and upper part of Bagaryshta subformation, on the other hand. Thus, nine schemes of sedimentary complex distribution can be compiled in total.

Some concerns were voiced about an excessively detailed analysis, and only 2-3 paleogeographic units were proposed. However, in doing so, we will inevitably distort actual relationships owing to the averaging of lithologically contrasted section intervals.

The Ai-Bol'shoi Inzer time. The onset of this time corresponding to the deposition of Navysh, Lipov, and Chudinka subformations of the Ai Formation and the major part of the Bol'shoi Inzer Formation was characterized by the existence of two large and rather contrasted zones (Fig. 4a). Coarse-clastic terrigenous continental and coastal-continental sediments were mainly deposited on the northeast; at the periphery of the Taratash salient the basic volcanics are embedded in this sequence (Fig. 5).

The basin was characterized by a variable depth increasing toward the southwest. At the same time, the sandy and silty-sandy sediments of lower and middle parts of the Bol'shoi Inzer Formation were deposited from high-density (?) gravity flows in the central meganticlinorium. They are referred to as deposits of a moderate depth. When the supply of sandy-silty material was interrupted, the fine-grained terrigenous sediments, slightly enriched in organic matter, were accumulated. Spatial relationships between sedimentary

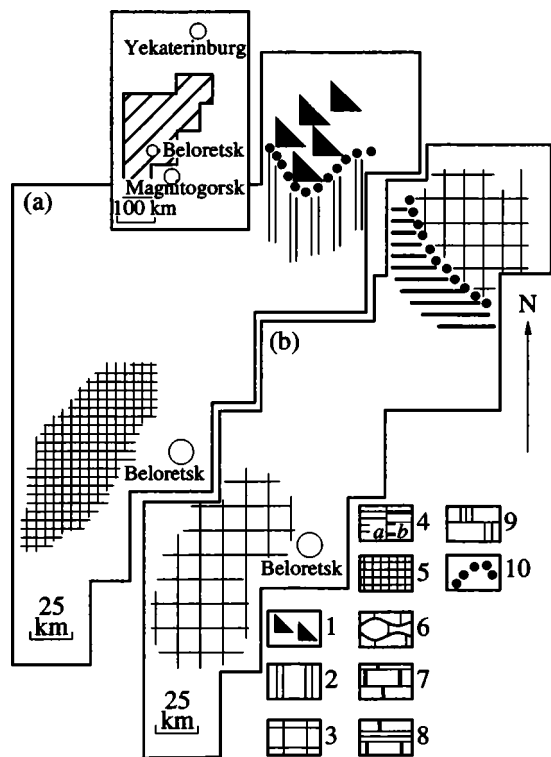


Fig. 4. Lateral relationships between sedimentary complexes at (a) early and (b) late Ai-Bol'shoi Inzer time.

Sedimentary complexes: (1) mainly continental, volcano-genic terrigenous and terrigenous rocks, (2) extremely shallow-water (coastal-marine and littoral) sediments, (3) shallow-marine terrigenous sediments, (4) distal fine-grained sediments: (a) ordinary, (b) enriched in fine-dispersed organic matter; (5) terrigenous, mainly sandy-silty sediments in distal and relatively deep-water zones; (6) coastal-marine carbonate sediments; (7) shallow-marine carbonate sediments, (8) terrigenous carbonate sediments of littoral and sublittoral zones, (9) marine proper (basin) carbonates; (10) inferred limits of complexes.

complexes of different origin and reconstructed lithofacies zones of the Ai-Bol'shoi Inzer section allow us to suggest that principal sources of clastic materials were situated on the northeast.

The composition of sandstones and conglomerates from the Ai and Bol'shoi Inzer formations (*Geologiya* ..., 1977; Kozlov *et al.*, 1989; Maslov, 1990; Maslov and Gareev, 1983; Yakobson and Kazak, 1978) indicates that metamorphic rocks of the Taratash salient, metamorphosed sedimentary rocks, acid volcanics and intrusive rocks served as provenances of that time. In three lower subformations of the Ai Formation, we dealt with contrasted lithological associations that in combination with a low maturity of clastic materials testify to a rapid accumulation and short distances of the clastics transport.

As inferred from the composition of sedimentary successions and volcanics, the paleotectonic environments of the Ai Formation deposition have been recently compared with present-day intracontinental

riffs, e.g., rift systems of the East Africa (Parnachev, 1982, 1987a, b; Parnachev *et al.*, 1986, 1990).

However, in my opinion, some relations argue against such an interpretation although the general sum of geological data seems to be reasonable for proposed correlation (Parnachev, 1987a, b). Firstly, in the Ai Formation we do not see a regressive succession, which is typical of volcanogenic sedimentary filling of rifts in eastern and northeastern Africa (Kaz'min, 1987; Nikolaev, 1986; Razvalyaev, 1988; *Vostochno-Afrikan-skaya* ..., 1974), which is assumed to be a model for geodynamic reconstruction. On the contrary, the bulk of sedimentary associations of the Ai Formation bears the pronounced transgressive character. Secondly, the paleogeographic reconstructions do not reveal the change in graben "polarity" that is characteristic of African rifts (Rosendahl *et al.*, 1992). Thirdly, the Ai Formation is devoid of undeniably recognized alluvial and closely related lacustrine sequences, which are indicative for continental rifts (Zonenshain and Kuz'min, 1993). Major and trace element composition of basalts from the Navysh Complex indicates that they are rather comparable with intraplate (including oceanic island) alkaline basalts (Maslov and Karstens, 1994). The lack of silicic volcanics also casts some doubt upon the direct analogy with alkaline basalts of bimodal volcanic series in East Africa and other intracontinental rifts.

Paleogeographic reconstructions for the eastern flank of the East European Platform and the western slope of the southern Ural (Maslov, 1994a, b) show that a large enough oval-shaped sedimentation basin or an embayment of a still larger basin existed at the territory under consideration in Early Riphean. Spatial interrelations between sedimentary complexes within this basin are stable and hence contradict the notion about the development of linear rifts and grabens with contrasted sedimentation.

Thus, lowermost Riphean deposits are probably related to so-called "boundary facies" that delineate the eastern limit of the sedimentation basin or a large island (?). The latter assumption seems to be more likely if the Transural Late Precambrian complexes are taken into consideration, but their age has been recently questioned (Ivanov, 1989); moreover, they are separated from western zones of the southern Ural by a suture of the Main Uralian Fault, and their strict paleogeographic setting in Early Riphean remains uncertain.

At the end of deposition of the Ai and Bol'shoi Inzer formations (Fig. 4b), the sediments probably filled a depression that previously existed in the central meganticlinorium. The upper part of Bol'shoi Inzer Formation bears clear indications of shallow-marine deposition (Maslov, 1993). On the northeast, the continental deposits were replaced by marine terrigenous sediments; i.e., the basin became appreciably wider and the shore line was shifted to the northeast (?).

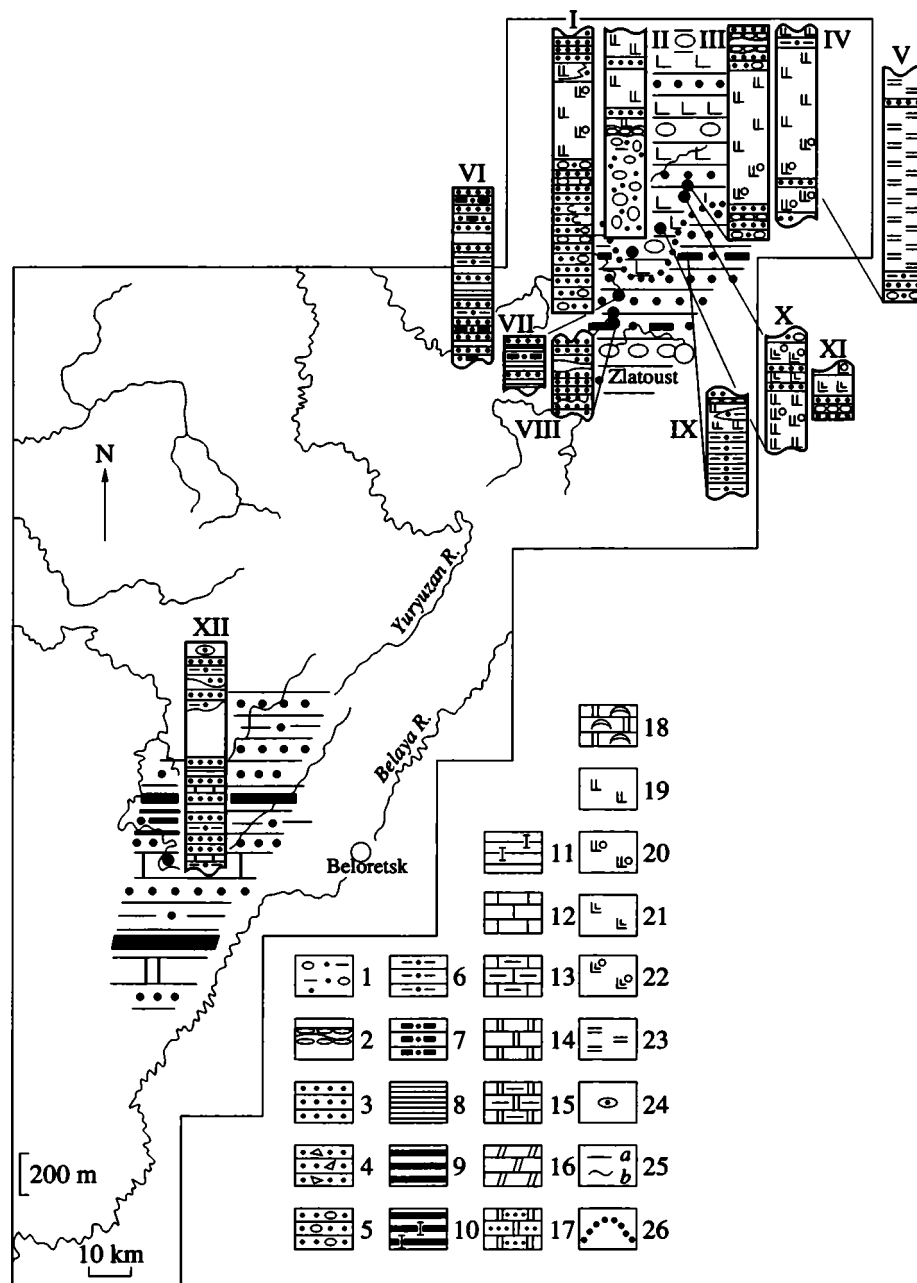


Fig. 5. Schematic lithofacies map of the Bashkirian Meganticlinorium for the early Ai-Bol'shoi Inzer time.

(1) Poorly sorted conglomerate-sand-clay deposits; (2) conglomerates and gritstones; (3) sandstones; (4) sandstones with interlayers of sedimentary flat-clastic carbonate and shale breccias; (5) sandstones with rare pebbles and gravels; (6) siltstones; (7) carbonaceous siltstones; (8) shales; (9) carbonaceous shales; (10) carbonaceous shales with terrigenous admixture; (11) carbonate shales; (12) limestones; (13) clayey limestones; (14) dolomites; (15) clayey dolomites; (16) dolomitic marls; (17) dolomites with terrigenous sandy-silty admixture; (18) stromatolitic dolomites; (19) trachybasalts; (20) amygdaloidal trachybasalts; (21) aphyric trachybasalts; (22) amygdaloidal aphyric trachybasalts; (23) greenschist rocks (altered basic volcanics); (24) rock lithology at unexposed intervals; (25) stratigraphic contacts: (a) direct contact with underlying or overlying deposits, (b) uncertain contact; (26) inferred limits of lithofacies zones.

The accessory mineral assemblage in sandstones of the Bol'shoi Inzer Formation indicates that the provenances of that time remained close in composition to the sources existing at the early Ai time (Kozlov *et al.*, 1989).

As follows from the composition of sediments and their facies appearance, the paleotectonic environments of the Ai-Bol'shoi Inzer time were most likely rather quiescent.

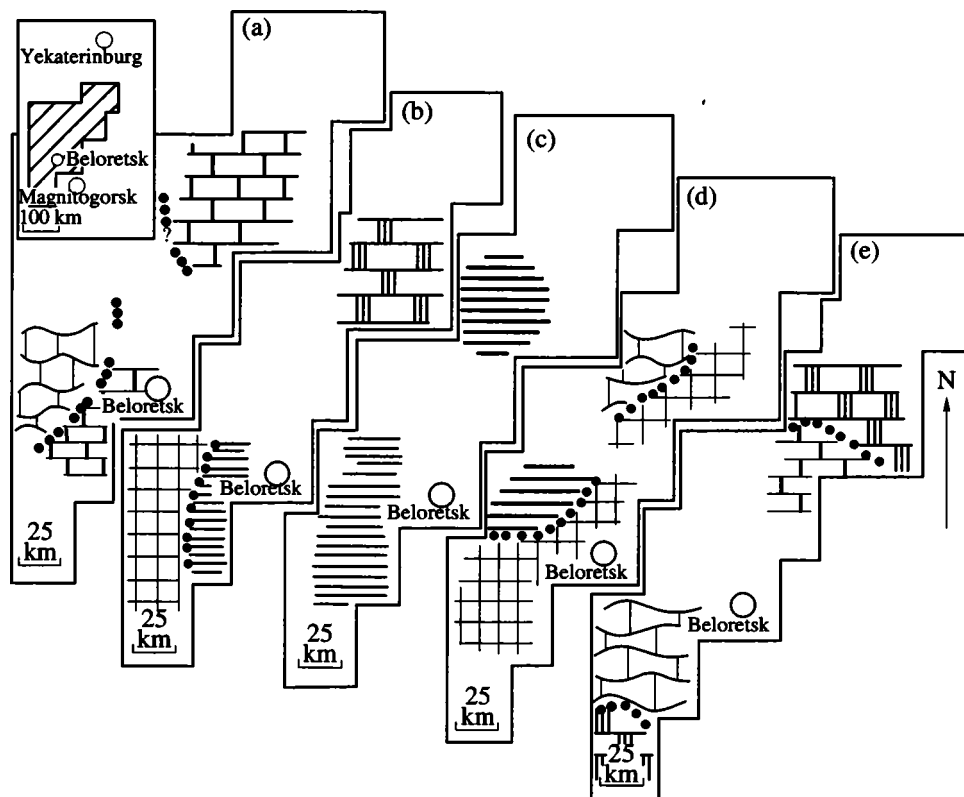


Fig. 6. Lateral relationships between sedimentary complexes at (a) Min'yak-Lower Kusa, (b) Berdagulovoulovo-Upper Kusa, (c) Polovinka-Angastak, (d) Lower Satka-Serdauk, and (e) Upper Satka-Lapyshta sublevels of the Satka-Suran level. Legend see in Fig. 4.

The Satka-Suran time. The deposition of basinal carbonate sediments was predominant at the territory under consideration in the Satka-Suran time. In addition, significant volumes of fine-grained terrigenous sediments were accumulated in central areas of the anticlinorium.

The thick complex of chemogenic dolomites, mainly of shallow-marine origin, was formed in the northeastern part of the meganticlinorium in early Satka-Suran time corresponding to lower Kusa and Min'yak subformations (Fig. 6a). Coastal carbonate sediments were deposited at the same time in the central meganticlinorium west of the Karatash Fault. Shallow-marine sediments were confined to eastern and southeastern parts of the territory. As inferred from the complex interrelations, the basin was deepened from the southwest to northeast. The thickness of sediments was increased in the same direction. Numerous interlayers and lenses of carbonate breccia with flat fragments in lower Kusa subformation were probably derived from allochthonous materials supplied from the southwest.

The deposition of basin facies proper occurred in the northeastern meganticlinorium during the late Kusa-Berdagulovo age (Fig. 6b). Some shoaling at the end of the preceding stage, which accompanied the

deposition of dolomites with *Kussiella kussiensis* Kryl. stromatolites, has been again replaced by a stable, quiescent, relatively deep-water (below the level of wave agitation level) carbonate sedimentation. It was interrupted by a supply of fine-grained carbonate material, by storm waves, and related processes. Dolomites of upper Kusa subformation are almost devoid of terrigenous admixture, suggesting a certain distal nature of their deposition. Mainly basinal sandy-silty-clayey and fine-grained terrigenous carbon-poor sediments accumulated in the central part of the territory. In this zone, the basin became deeper probably from the west to the east; the clay material content gradually increased in the same direction.

The Polovinka-Angastak age was characterized by an almost ubiquitous deposition of fine-grained terrigenous sediments (Fig. 6c). On the northeast these sediments were somewhat enriched in fine-dispersed organic matter whereas in the center of meganticlinorium the sections of this level are mainly represented by bluish-grey and bluish-green shales and fine-grained siltstones. The correlation of Angastak subformation (Suran Formation) sections at the latitude of the Ishly settlement indicates that the fine-grained terrigenous material in the given part of the basin was derived from the west. As can be seen from the lithofacies map at a

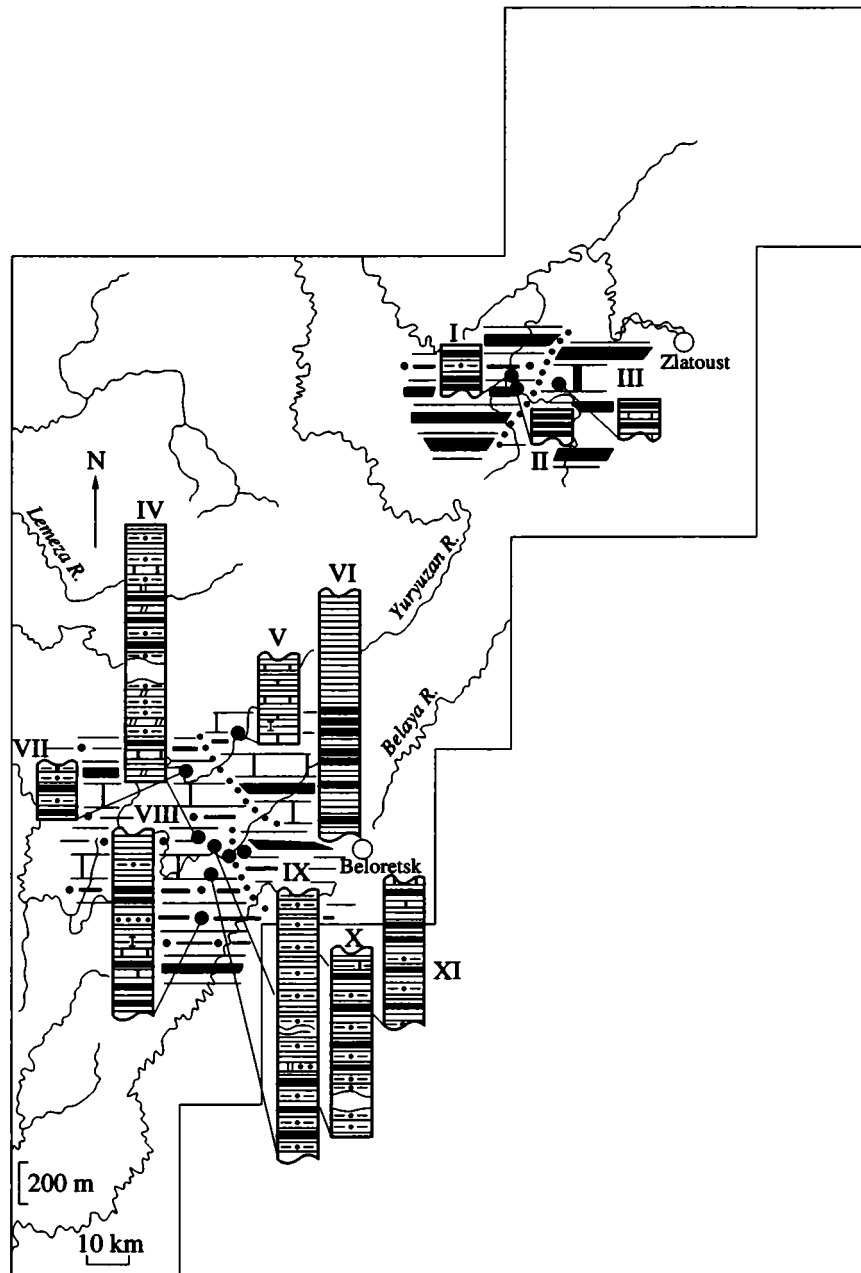


Fig. 7. Schematic lithofacies map of the Bashkirian Meganticlinorium at the Polovinka-Angastak stage. Legend see in Fig. 5.

scale of 1 : 500000 compiled for this level, the most fine-grained terrigenous sediments with rare limestone interlayers are confined to the upper reaches of Bol'shoi and Mali Inzer rivers. The content of silty and fine-grained sandy materials gradually increases westward and southwestward (Fig. 7). As opposed to the Min'yak-early Kusa age, the middle of the Satka-Suran time was characterized by a reverse thickness distribution: the greatest thicknesses were confined to the central part of the Bashkirian Meganticlinorium.

In the late Satka-Suran time corresponding to the formation of terrigenous and carbonate deposits of lower Satka and Serdauk subformations, the system of terrigenous material supply was apparently changed. Two large sedimentary complexes are recognized in the lower Satka subformation in the northeastern meganticlinorium (Fig. 6d). On the eastern side, shallow-marine silty shales are rimmed by the carbonate sediments enriched in terrigenous material and containing various structures of coastal-marine origin. Based on the above relationships, the western facies are sug-

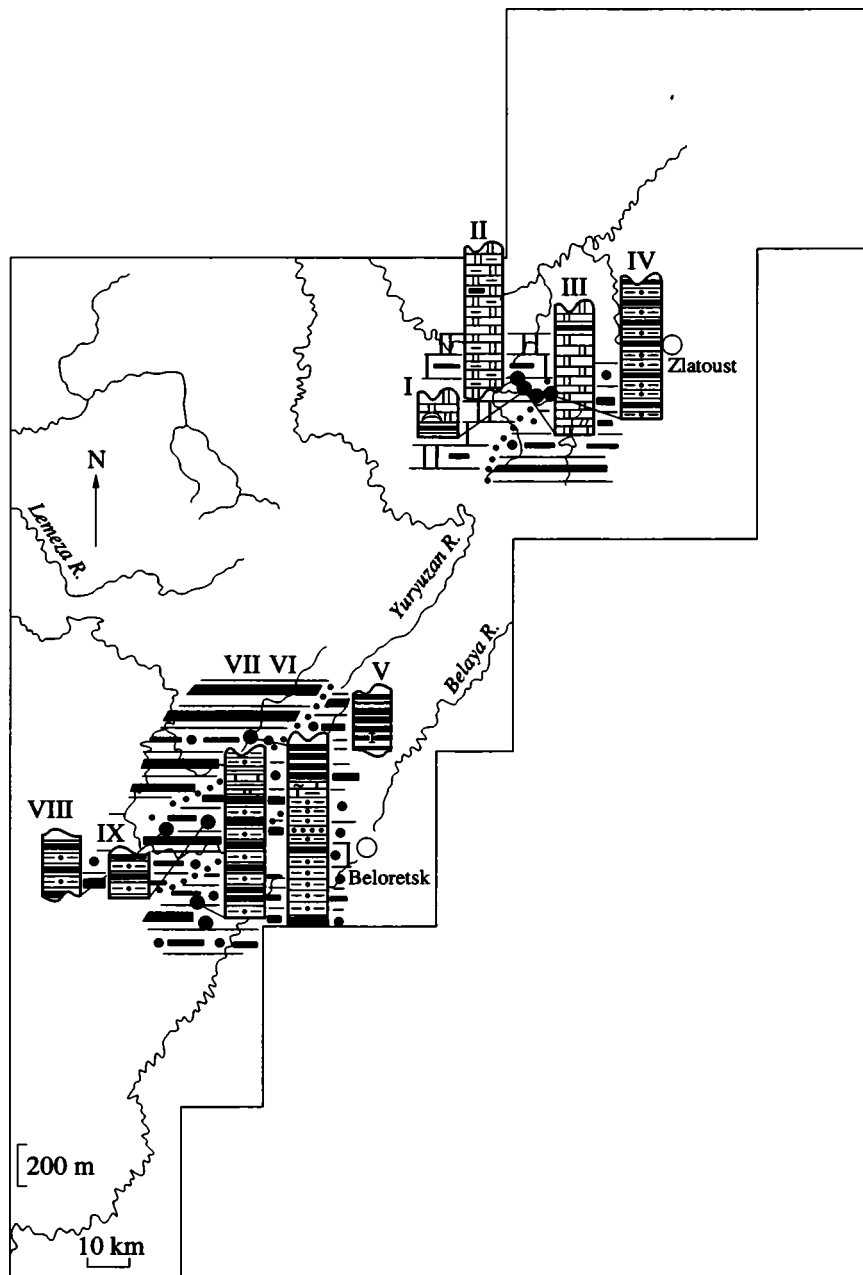


Fig. 8. Schematic lithofacies map of the Bashkirian Meganticlinorium at the early Satka-Serdauk stage.
Legend see in Fig. 5.

gested to be more distal. At the latitude of the Beloretsk town, most distal facies, which are represented mainly by fine-grained terrigenous sediments enriched to some or other degree in fine-dispersed organic matter, are also related to western and northwestern zones (Maslov and Krupenin, 1991), whereas to the east and southeast the shallow-water marine sandy-silty-clayey sediments are predominant (Fig. 8).

The end of Satka-Suran time, i.e., Lapyshka-late Satka age, was once again marked by a predominant accumulation of carbonate sediments throughout the

entire territory (Fig. 6e). On the northeast these are basal carbonates (limestones and dolomites) with numerous flat-clastic breccia layers; they are replaced southwestward by shallow-water marine carbonate deposits. Dolomites with a terrigenous admixture, various flow structures and flat-clastic breccia are predominant in the Lapyshka subformation at the middle reaches of the Bol'shoi Inzer River in central Bashkirian Meganticlinorium (Maslov, 1993; Maslov and Krupenin, 1991). Southward they are replaced by dolomites with shale and carbonaceous shale interlayers

and thin phytogenic beds, which were apparently formed under more quiescent offshore (?) conditions. The comparison of facies features of the Lapyshya subformation (Suran Formation) near the Kartalinskaya Zapan', Lapyshya, and Askarovo villages and the Aigir station allows us to suggest that the fine terrigenous clastics were derived from the north and northeast.

The paleotectonic regime of the Satka–Suran time is interpreted by most researchers as quiescent platformal (depressional) type (Ivanov *et al.*, 1986; Kurbatskaya, 1985; Parnachev, 1982, 1987a).

Bakal–Yusha time. Terrigenous sediments of shallow-water and proper marine origin were predominant at the given stage of evolution; a specific complex of intercalating sublittoral and littoral terrigenous and carbonate deposits was formed at the end of this stage.

The paleogeography at the early Bakal–Yusha time was mainly determined by shallow-water environments almost throughout the entire Bashkirian Meganticlinorium (Fig. 9a). Some local districts favorable for deposition of sediments slightly enriched in organic matter can be delineated within the zone of shallow-water sedimentation on the basis of lithotype relationships (Fig. 10).

On the northeast of the structure the shallow-water sediments were probably replaced by more deep-water, fine-grained, and significantly thick terrigenous sediments enriched in fine-dispersed organic matter (Makarovo subformation of the Bakal Formation). Spatial relationships between complexes allows us to suggest that areas located to the southwest and west from the Bashkirian uplift could serve as sources of clastic materials.

To the end of Bakal–Yusha time, when the Malobakal subformation (Bakal Formation) and upper parts of Bagaryshya and Berdagulovo subformations (Yusha Formation) were deposited, the main changes in paleogeographic environments took place on the northeast where the complex of terrigenous and carbonate rocks was formed (Fig. 9b) under more shallow-water conditions as compared with underlying strata. According to Krupenin's data (Krupenin, 1986a, b; Parnachev *et al.*, 1990), deposits of upper subformation of the Bakal Formation are typically characterized by the presence of rhythmic, gradational, wavy, cross (uni- and diversidirectional), and cross-wavy bedding, small erosional pockets and channels, ripple- and flow-marks, desiccation fissures, breccias with angular flat fragments of shales, convolute structures, etc.

The reconstruction of facies environments of initial sedimentation indicates that this complex is mainly represented by coastal-marine and lagoonal deposits; proper basinal distal facies are developed to a considerably less extent. As many researchers assume, the frequent alternation of carbonate and terrigenous sedimentational modes at the end of Bakal time expressed in multifold intercalations of limestones, dolomites, and silty shales in the Malobakal subformation testifies to a relatively unstable tectonic regime and to an onset

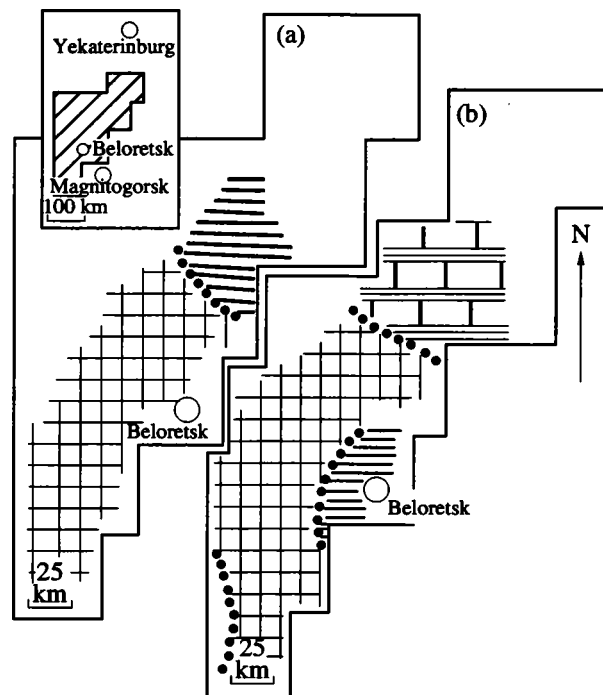


Fig. 9. Lateral relationships between sedimentary complexes at the Bakal–Yusha level: (a) Makarovo–early Yusha stage and (b) late Bakal–late Yusha stage.

Legend see in Fig. 4.

(?) of gradual regression (Garan', 1969; *Geologiya ...*, 1977).

The formation of the terrigenous–carbonate complex of the Malobakal subformation and the paleogeography of the northeastern meganticlinorium at that time were comprehensively studied by Krupenin (1983, 1986a, b, 1991). Up to six cycles were recognized within the complex; the lower levels of each cycle are represented by terrigenous sediments of on- and offshore shallow-marine facies, whereas the upper levels are composed of calcarenites, chemogenic and phytogenic carbonates of shallow-water marine origin. The grain size of terrigenous units is successively decreased upward from one cycle to another; the role of carbonate interlayers is increased, and the facies composition of sediments is changed. While sandy and sandy–silty–clayey sublittoral and coastal-marine facies are predominant among terrigenous rocks in lower part of the complex, the fine-grained sediments of distal shallow-water facies are widespread in the upper part.

The analysis of facies zone migration at the late Bakal–Yusha time allowed Krupenin (1986b) to reconstruct the position of provenances for the northeastern Bashkirian Meganticlinorium. The provenances were located mainly on the south at the initial stage of terrigenous–carbonate complex formation and on the north at the final stage (post-Shuida time). Krupenin has suggested that such disposition of provenances may indicate a sublatitudinal elongation of sedimentation basin

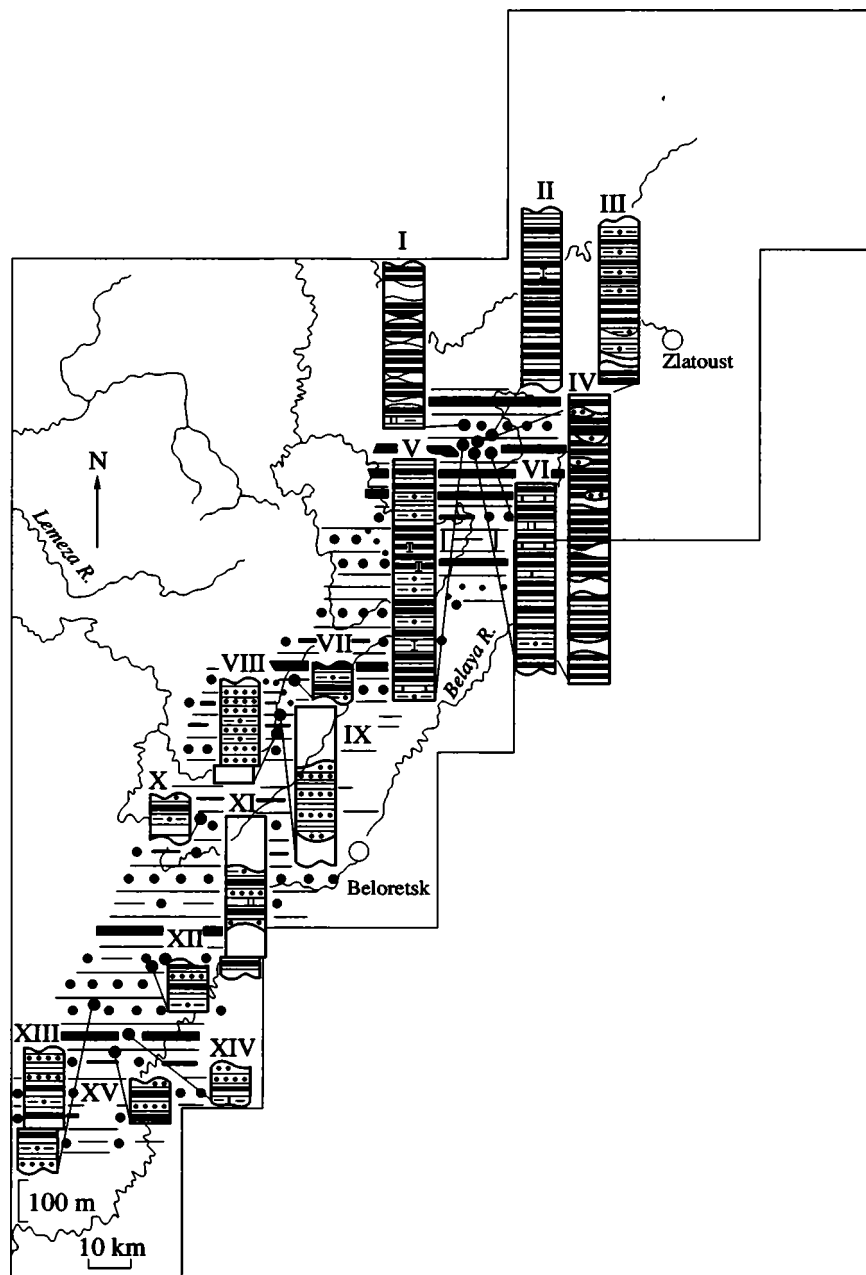


Fig. 10. Schematic lithofacies map of the Bashkirian Meganticlinorium at the Makarovo-early Yusha stage. Legend see in Fig. 4.

of the Bakal-Yusha time. The facies composition of sediments and the structure of the upper part of the Bakal Formation confirm the previous statements of M.I. Garan' about a "mature" tectonic relief of outer parts of the basin at this stage and suggest a general quiescent paleotectonic regime with local cyclic secular (?) fluctuations (Anfimov, 1982; Krupenin, 1986b).

In central Bashkirian Meganticlinorium the late Bakal-Yusha time (late Bakal-late Yusha age) was noted for an insignificant change in the paleogeographic situation as compared with its onset. At this

time the area occupied by sandy-silty-clayey sediments of shallow-water marine origin was slightly reduced and some small sites with relatively fine silty and silty-clayey sediments, often organic matter-bearing, arose in the offshore zone. They were probably supplied by provenances located in the central part of the meganticlinorium. It seems likely that these provenances also supplied the clastic materials northeastward where the terrigenous-carbonate complex of Malobakal subformation was formed. As was mentioned above, Krupenin's data are partly consistent with this

interpretation. The Korelka Sequence area located to the south and southeast from the Bakal–Satka district probably served as another source of terrigenous materials. According to Parnachev *et al.* (1986) and our own observations, the silty–clayey, silty and silty–sandy sediments of the Korelka Sequence were deposited under shallow-water marine conditions.

Characterizing the environment of the Bakal Formation deposition in general, Parnachev *et al.* (1986) indicate that stromatolitic carbonates, traces of erosion, and synsedimentation breccias testify to the deposition of initial sediments in the environment characterized by the alternation of the open shelf and carbonate platformal conditions with lagoons and tidal zones. However, the special works on stromatolite formation conditions in Early Riphean sedimentation basin of the southern Ural show that the stromatolites are related only to basin sediments and were formed in quiescent relatively deep-water zones (Maslov and Kuleshova, 1988). Their spatial distribution does not give obvious evidence in favor of ... *clear recognition of stromatolitic reefs* ... both in Bakal–Yusha and Satka–Suran times (Parnachev, 1986; Parnachev *et al.*, 1990).

CONCLUSION

The data obtained lead to certain conclusions concerning the provenance and sedimentation areas and the general evolution of the eastern flank of Volga–Uralian sedimentation basin in Early Riphean.

The composition and relief of the provenance are most surely reconstructed for the early Ai–Bol'shoi Inzer time. Numerous conglomerate beds, interlayers, and lenses in the Navysh, Lipov, and Chudinka subformations of the Ai Formation, the generally poor sorting of clastics, sharp facies changes and some other features indicate a rather rugged relief of the land adjoining the sedimentation area. This land was composed of various metamorphosed (gneisses, crystalline schists), igneous and metasedimentary rocks. The deposition at early Ai–Bol'shoi Inzer time occurred under both subaerial and subaqueal conditions. Continental, sedimentary and volcanogenic sedimentary deposits were apparently characteristic only of the northeastern Bashkirian Meganticlinorium. Southwestward they were replaced by coastal-continental and coastal-marine deposits. A moderately deep-water (?) zone where mainly sandy and sandy–silty sediments were accumulated is outlined in central part of the meganticlinorium. Clastic materials were transported into this zone mainly by grain flows that repeatedly interrupted the accumulation of terrigenous muds.

Basinal shallow-marine and coastal-marine terrigenous and carbonate complexes of Satka–Suran and Bakal–Yusha ages were deposited within a common sedimentation basin. The provenance area was almost completely flattened, located far enough and served as

a source of fine-grained terrigenous (mainly pelitic) material.

Reconstructions of lateral relationships between sedimentary complexes and the analysis of lithofacies maps do not confirm the assumption that a great number of small basins existed at the territory under consideration in Early Riphean. On the contrary, except in the lower Ai level (Navysh, Lipov, and Chudinka subformations of the Ai Formation) the Burzyan Group is devoid of so-called “boundary” facies or complexes, which could be regarded as indicators of coastal zones or areas of continental sedimentation. In present-day contours of the Bashkirian Meganticlinorium the deposits of upper Ai, Satka, and Bakal levels are represented by a combination of basinal sediments that testifies to a larger sedimentation area as compared to the territory considered in this paper. The suggestions about the lack of large long-lived synsedimentation troughs and uplifts within the limits of now-existing Bashkirian Meganticlinorium during Early Riphean, as well as about a significant migration of paleogeographic zones are not corroborated.

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The Silicification Processes in the Paleogene Sands of the East European Platform

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Abstract—Quartzitic-like sandstones are widespread in the Paleogene deposits of the East European Platform. The content of siliceous material is 20–25 vol %. Two genetically different sources of silica in the sandstone matrix are recognized. The first source is related to postsedimentary transformation of sand-overlying bentonites, opokas, or siliceous clays that supplied free silica. The second source is related to the hydrothermal silica inflow through conduits and the thermal water discharge in near-bottom areas of sedimentation basins.

INTRODUCTION

Lenses, layers, or beds of quartzite-like sandstones are widespread among the Paleocene–Eocene deposits of the East European Platform. They often armor erosional outliers of Early Cenozoic loose deposits, form stratified interlayers within sedimentary sequences, or sometimes occur in the form of vertical dikes. The problems of siliceous matrix origin and silica sources are the most difficult to solve during the reconstruction of a genesis of quartzite-like sandstones. Direct calculations of thin section areas occupied by a siliceous matrix give the knowledge of the content of authigenic silica in quartzite-like sandstones from different objects studied (Table 1).

At a host sand porosity of up to 30%, the enclosed quartzite-like sandstones have a porosity of 2 to 5%; i.e., the amount of authigenic silica is up to 20 to 25%. The observations show that the cementation of sands is independent of their grain size but is most prominent

only in well-sorted quartzose and quartz–glauconite sands. We have not found the silicified clay–sand varieties among the Paleogene sandy rocks developed in the Dnieper–Donets Basin, Don and Volga river basins, Obshchii Syrt, Mugodzhary region, and Northern Aral region. Thus, the initial sedimentational contamination of sands by fine-dispersed material makes impossible their further cementation with free silica. The established regularities in the formation of quartzite-like sandstones testify to the significance of such a parameter as parent-rock permeability.

Our studies of quartzite-like sandstones, carried out over the vast areas of the East European Platform and adjacent regions, have shown that their morphology, genesis, and stratigraphic position within sedimentation cycles are often changeable in different sections. Therefore, it is imperative to describe various types of sandstones and to discuss the problem of their genesis.

Table 1. Composition and type of matrix in quartzite-like sandstones

Sample no.	Location	Cement composition and type	% of a thin section area	
			pore	matrix
80/70	Mamon quarry near the Don River	Opal, cristobalite lepispheres; pore filling	12	10
81/70	"	Opal; pore filling	6	18
82/70	"	Opal, chalcedony; pore filling		
270/70	Ichka Mount, Obshchii Syrt	Lussatite; filmy, crustified	3	18
172/75	Tashly quarry, Ul'yanovsk oblast	Opal; pore filling	1	20
342/70	Kunduzu-Sai gully, Mugodzhary region	Lussatite; filmy, crustified	5	18
282/72	Kostenets gully, Kanev	Lussatite; filmy, crustified	3	20
347/70	Aulia River escarpment, Mugodzhary region	Two generations of lussatite; crustified; chalcedony; pore filling (Figs. 2b and 2c)	6	20
K-103	Lob outlier near Kamyshin	Quartz; regeneration (Fig. 2d)	2	22
K-43	Gully near the Lobachi farm	Opal; pulp structure (Fig. 2e)	n.a.	80

LITHOLOGICAL FEATURES OF QUARTZITE-LIKE SANDSTONES

Stratal sandstones are distinctly divided into two types by the character of their structure. The first type includes asymmetric bodies forming cemented sheets overlying thick sequences of loose sands. Such layers have a flat top and irregular bottom (Fig. 1a). The quartzite-like sandstone layer studied in the Mamon-on-Don quarry belongs to this type. The layer thickness amounts to 4 m, but sands are often loose at a number of places within the quarry, and the quartzite-like sandstone sheet looks as if it is pierced. But even in the areas in which the upper sand sequence is cemented and represented by quartzite-like sandstone, the layer thickness is variable and depends only on the configuration of a sandstone bottom. The sandstone layer overlapping the sequence of loose sands in the Tashly quarry, Ul'yanovsk region, as well as sandstones from the Ichka Mount in the Obshchii Syrt belong to the same type.

In all cases described, the loose sand sequences overlapped by quartzite-like sandstones are further overlain by the layers of opokas (Tashly quarry) and bentonites (Ichka Mount) or semiloose silt-like rocks with the X-ray amorphous main rock-forming mass (Mamon quarry). In the last case, only free oxyhydroxides are present in the composition of amorphous mass that produces only intense halo in an XRD image. In the Mamon quarry section, the composition of pelitic component of the silt-like layer (sample 84) is as follows (in %): SiO_2 49.82, TiO_2 0.47, Al_2O_3 10.98, Fe_2O_3 17.02, FeO 0.19, CaO 1.16, MgO 1.16, MnO 0.03, Na_2O 0.14, K_2O 1.44, H_2O^+ 8.18, H_2O^- 7.46, CO_2 0.45, C 0.08, and P_2O_5 1.09; it is noteworthy that the amount of SiO_2 removable by twofold soda extraction accounts for 17.49% in this sample. The above composition does not reflect the initial rock composition; this is merely the remain of the substance that supplied free silica for cementing the underlying sands.

Thus, the asymmetric layers of quartzite-like sandstones represent a kind of interface between the loose sands and overlying rocks, whose post-sedimentation changes are accompanied by the release of abundant free silica. In these cases, the cementation of the sand top may be caused by penetration of silica from the overlying layer into the near-contact zone. Not only the form of the bottom of the secondary cementation zone, but also the type and amount of matrix in the sandstone profile speak for such a conclusion. Thus, in the Mamon quarry, sample 80 was taken from the sandstone bottom, sample 81 was taken from its middle section, and sample 82 was taken from the top section. The minimum porosity and the presence of chalcedony within the pore space are typical of the top section. In the middle section of the layers, the matrix is still rather abundant, but it is homogeneous, and its whole mass is represented only by opal. In the bottom section, sandstone is looser, and the pore space is only half-

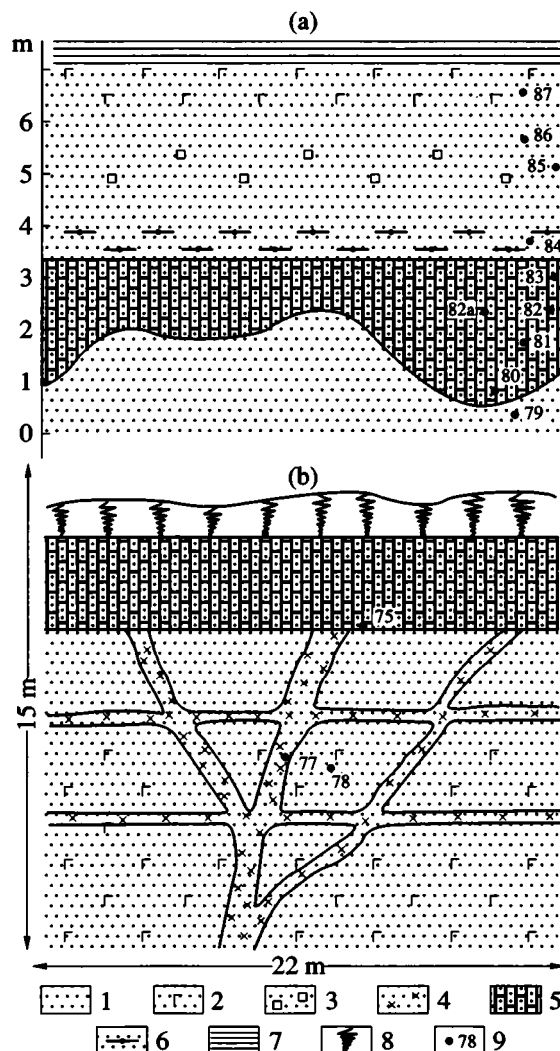


Fig. 1. Morphology of quartzite-like sandstones and their location in the Paleocene sections. (a) Near the Mamon settlement, Don River, (b) near the Grigorovka village, Dnieper Region. (1) quartz sands, (2) quartz sands with glauconite, (3) ferruginous sands, (4) compact sands with opal and glauconite segregations, (5) quartzite-like sandstones, (6) silts, (7) clays, (8) soil-plant cover, and (9) sample location and no.

filled with opal. The individual matrix masses are isolated in the form of lepispheres.

Such a matrix structure testifies to the downward percolation of cementing solutions supersaturated with silica, rapid formation of SiO_2 gel, and its dispersion (isolated lepispheres) in the lower cementation zone. In this case, the upper sand zone was as a gradually choking filter through which the dispersed phase (SiO_2 gel) penetrated. The last solution portions could not penetrate through the choked filter and were deposited in a residual pore space of the upper zone in the form of chalcedony; i.e., the regime of excessive SiO_2 precipitation changed at the final cementation stages (Murav'ev, 1975). If at rather high sand permeability in

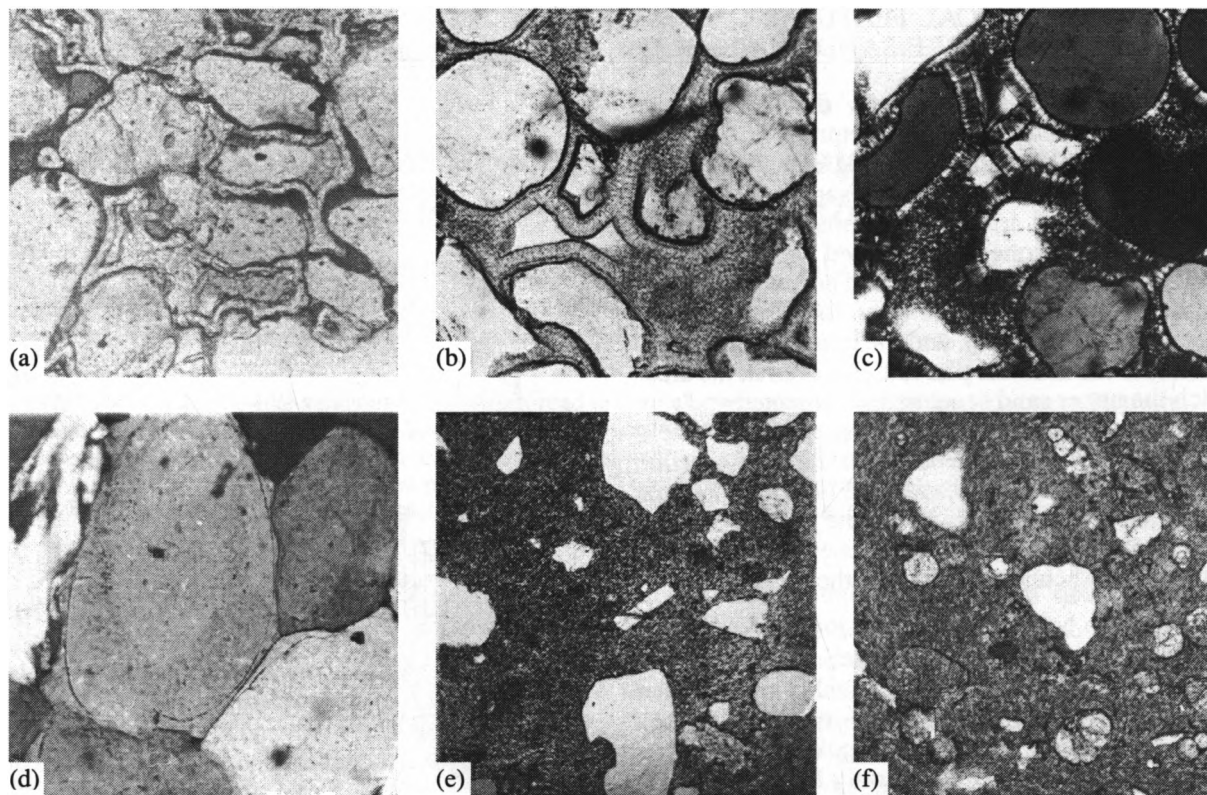


Fig. 2. Silicification structures in thin sections. (a) Senomanian, (b)–(f) Paleocene. (a) The Senomanian sand silicified in the top section with lussatite crustification rims in matrix and residual pores filled with opal. Sample 34, the section near the Lobachi farm. Transmitted light, magn. 100; double lussatite rim border on fragments and chalcedony filling of residual pores in sandstone. Sample 375, section at the Aulia River, the Mugodzhary region: (b) transmitted light, magn. 50, (c) crossed nicols, magn. 50; (d) quartzite with a mosaic texture and pore space is filled with regeneration quartz. Sample 168, Lob outlier near Kamyshin. Crossed nicols, magn. 100; (e) pulp structure in the dike of a sand–opal composition. Sample 51, section near the Lobachi farm. Transmitted light, magn. 50; and (f) silicified chalk with shells of foraminifers replaced by opal. Sample 37, section near the Lobachi farm. Transmitted light, magn. 50.

the initial stages, colloidal solutions and SiO_2 gel penetrated to a considerable depth from the layer top (up to 4 m) and occupied virtually the whole pore space, then the process of pore space filling with new silica portions was delayed with gel aging. In the top section, the residual pores were filled like geods, i.e., by means of SiO_2 diffusion through residual microchannels (Grigor'ev and Koryakina, 1962).

Many quartzite-like sandstones are characterized by the following important feature: two and sometimes three generations of cementing siliceous material are successively overlapped on clastic grains (Figs. 2a–2c). Different matrix generations may be represented by various mineral modifications of free silica, e.g., opal and lussatite (Fig. 2a) or lussatite and chalcedony, which sometimes form two rims on clastic grains (Figs. 2b and 2c), etc. Finally, the matrix of quartzite-like sandstones may be represented by zonal rims of authigenic quartz.

The second type of stratal sandstones is represented by symmetrical lenticular bodies within continuous sand sequences. They form the series of stratified bun-shaped bodies and lenses (hereinafter, stratified lenses). The traces of ancient erosion are not observed above

such sandstone interlayers (within sands); moreover, the common sand and sandstone textures are traced through the sand–sandstone interfaces. The central zones of stratified lenses have a maximum density. Sandstones from the Kunduzdy-Sai, Kaney, and Aulia River regions (Table 1) belong to this type.

The source of matrix-silica is not clear in such layers, but the mass of authigenic SiO_2 is very large; in any case, it is commensurable with the clastic mass of quartzite-like sandstones. The cement is almost absolutely absent in host loose sands; therefore, the selective cementation only of certain levels deserves special attention.

The extremely large but occasional silica supply into the sedimentation basin should be explained. We should pay attention to the localization of thick quartzites only in narrow zones, whereas only a fan of stratified lenses is traced beyond these narrow zones. Thick (about 22 m) quartzite-like sandstones are developed in the Kuchura and Skugareevka quarry district, Ul'yanovsk region; beyond these quarries, the synchronous sequence of quartz sands contains only a few sandstone layers that further pass into a series of stratified lenses. The zone

of transition of continuous quartzite-like sandstones into sands with stratified sandstone lenses has a thickness of no more than 200–300 m. In this zone, the quartzite sequence is sharply separated by loose sand interlayers into a series of bods. At the same time, the cementation type abruptly changes. The complete pore filling is observed only in the central zones of stratified lenses, and the streamline-flow pattern of the stratified lens center is observed. Within each zone, the degree of cementation successively decreases from the center to the periphery of a stratified lens.

The complexly built body of cemented sandy rock represents a thick lens at the center. At some stratigraphic levels, the lens is complicated by layers stretching far from the central body into loose sands. Based on these observations, we can suppose that the source of free silica operated for a long time within the zone of development of a central body. A different temporal intensity of free SiO_2 inflow was registered by the lateral extension of cemented sandy rocks at each stratigraphic level.

The similar interpretation of the genetic nature of quartzite-like sandstone cementation implies the existence of a local SiO_2 source, i.e., requires the assumption of a hydrothermal inflow of water hypersaturated with dissolved silica. This source should have operated for the whole time of formation of quartzite-like sandstones, though its intensity was evidently time-dependent. The amount of silica precipitated in the zone of sand cementation is commensurable with the mass of clastic material and accounts for about a quarter of a rock volume.

SECTION TYPES

The development of a secondary vein silicification in loose sand sequences may illustrate the principal possibility of hydrothermal SiO_2 inflow. Similar phenomena were described in the Grigorovka village region at the Dnieper River right bank, near Kamyshin at the Volga River right bank, and near the Lobachi farm in the Don–Khopr interfluvial area (Fig. 3).

The Dnieper region. In the gully north of the Grigorovka village, one can observe the sandstone vein intersecting the sand sequence of the Eocene Buchak Formation (Figs. 1b and 3). The glauconitic sand unit (10 m) is revealed in the bottom section. In the upward 10-m interval, the glauconite content in sand gradually decreases and tends to zero.

The sand unit is crosscut from bottom to top by a set of inclined branching veins discernible in the outcrop wall by a more intense green color and stronger cementation. The thickness of the major vein ranges from 10 to 15 cm, and that of the subsidiary veins accounts for 3.5 cm. Additionally, sandstone veinlets are observed parallel to the bedding. They are distinctly noted by coarse sand interlayers and other features similar to that of the main vein body, i.e., an intense green color and a relatively higher degree of cementation.

The microscopic analysis of sandstone from the vein body has shown that numerous globular opal particles (from 3 to 10 μm in size) appear in their pore space. Moreover, the overgrowth rims also composed of a glauconite material are found in the contact zones of glauconite grains. Such rims are only locally developed along the contact with adjacent grains. Thus, there originates additional pore matrix ensuring relatively higher rock strength. Loose sands are observed beyond sandstone veins and subsidiary veinlets.

The intrusion of loose sand sequences by dikes without apparent displacement may be related to the availability of a local hydrothermal source below loose sands, i.e., to the origination of an unconsolidated permeable zone without any appreciable displacements of rock blocks relative to one another. However, the participation of silica-supersaturated thermal water is evident in this case. Here, the upper unit of quartzite-like sandstones may be considered as a syngenetically cemented upper zone of sands in the hydrothermal water discharge zone.

The degree of cementation of a sandstone unit differs from top to bottom, and the unit can be divided into three layers separated by the discontinuous zones of loose sands with a thickness of 3 to 10 cm. Sandstones serve as the shielding surface overlain by thin eluvium layer, but their structure does not allow considering them as an asymmetric sand layer, over which some unknown layer, the source of SiO_2 (bentonite, opoka), existed and was destroyed by latest erosion. As it has been indicated, the quartzite-like sandstone member is composed of three layers overlying one another and separated by zones of less intense cementation or loose sand lenses.

It is of importance to point out that the segment under consideration is located within the specific tectonic junction (Fig. 3) with a series of different-direction deep faults (the Kanev, Kiev, Mogilev–Podol'skii, Uman, and Pervomai) converging in its crystalline basement (Karta ..., 1978). The tectonic movements along these faults continued in the Paleozoic, Mesozoic, and Cenozoic and were possibly accompanied by hydrothermal activity.

The Middle Volga region. Here, the dike-shaped siliceous bodies cutting the Kamyshin Formation sands are identified in the sections of three erosional outliers located at a distance of 8–10 km north-northwest of Kamyshin. The outliers have the form of truncated cones, two of which are called Ushi, and the third of which is called Lob. They have a height of 30 to 40 m, a bottom diameter of 200 to 400, and a top diameter of 100 to 150 m.

The outliers have a uniform geological structure. The sequence of monomictic quartz sands of the Kamyshin Formation is crosscut by a series of subvertical siliceous dikes (Figs. 4a and 5a) composed of quartzites and quartzite-like sandstones with a thickness of 15–30 cm to 2 m.

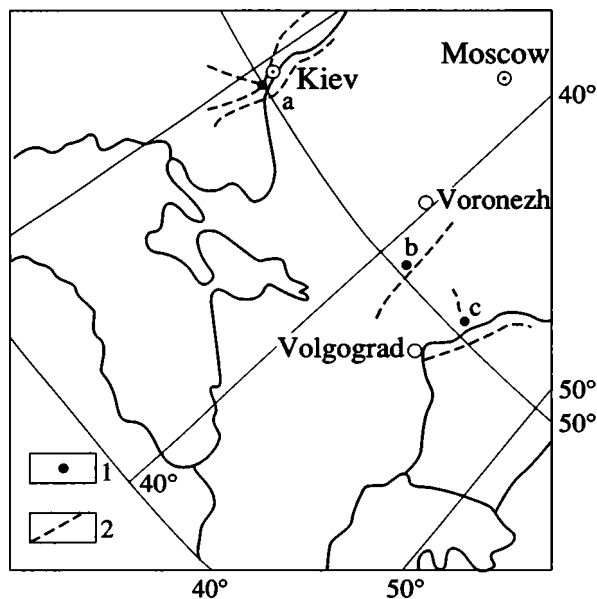


Fig. 3. Location of hydrothermalites with conduits and faults in the basement. (1) Objects: (a) near the Grigorovka settlement, Dnieper region, (b) near the Lobachi farm, Don-Khoper interfluve, and (c) near Kamyshin, Volga Region; (2) large faults in the basement.

In plan, the dike system forms a complex network of intersecting bodies. In the upper section, certain dikes are terminated by bun-shaped bodies from 0.1 to 0.4 m in size; however, the main part of the dikes are traced up to the outlier summits where they are thickened and further (upward the section) change into horizontal lenses with numerous, branching veins and tubular bodies of quartzites and quartzite-like sandstones (Figs. 5b–5h). The tubular bodies (Figs. 5e–5h) are composed of the exterior (quartzite-like) and interior (semiloose) sandstone zones and often have a cup-shaped form. The vertical migration of solutions probably promoted the cementation of channel walls not affecting the permeability of channels themselves.

In plan, the system of such bodies has the augen or ring-shaped structures; occasionally, they are converged (Fig. 5f). Tubular segregations are also encountered (Fig. 5h). The morphologically similar tubular, veined, lenticular, or vein-layers bodies are described in the study of a hydrothermal–fractureless vein formation (Pospelov, 1963; Pospelov and Kushanskaya, 1962). Bodies of similar morphology are also described in the zones of elision water discharge (Glazovskii, 1976; Kaleda and Lipaeva, 1992; Kholodov, 1991; Mashkovtsev *et al.*, 1969).

The petrographic structure of quartzites and quartzite-like sandstones studied in the Lob outlier section is characterized by a virtually complete filling of the pore space with regeneration quartz (Fig. 2d). The clay component is virtually absent in sandstones, and their residual porosity is 1–6%. Thus, up to 20–25% of a quartzite mass is represented by authigenic quartz. The data on

chemical composition of the Lob outlier quartzite are presented in Table 2 (samples G-33, 183, and 185) in comparison with loose sands from the Balberka quarry. The initial mass of quartz grains is well-washed; the grain surface are free of films of ferruginous or clay material. Regeneration quartz always retains the optic orientation of a quartz core (fragment). In this case, the originating structure is mosaic (Fig. 2d). Only sometimes, we can observe the clastic grain contours within the regenerated grains. Such a complete quartz cementation may develop only in case of growth of regeneration crystalline quartz on account of silica from true solutions. The participation of siliceous gel is ruled out in these cases.

The characteristic feature of quartzite-like sandstones from the Ushi outlier, which are apparently similar to the above-mentioned varieties from the Lob outlier, is the appearance of imprints of the known Late Paleocene flora (Baikovskaya, 1984; Makulbekov, 1977) in a flora-bearing lens within the upper section. The petrographic study of flora-bearing quartzite-like sandstones from the Makulbekov's collection indicates that they differ from the Lob outlier rocks by the presence of feldspars (up to 1%) and minor redeposited glauconite. It is also established that these sandstones are cemented by opal-CT and chalcedony. Opal-CT (lussatite) forms distinct crustification rims on both quartz fragments and glauconite grains. The residual pore space is filled with chalcedony.

Because the preservation of leaf flora is strictly governed by absence of rewashing and extremely rapid cementation of sands, we can suppose that the flora-bearing layer was formed in synchronism with its cementation by siliceous gel. Moreover, the change in sand composition (the appearance of feldspar and glauconite admixtures) testifies to the origination of a new source of clastic material that supplied feldspars and glauconite. In the neighboring Balberka sand quarry, the participation of a similar terrigenous source and origination of an opal–chalcedony cement in sandstones is revealed in the base of the latest sedimentation cycle in the Kamyshin Formation top. Therefore, we can suppose that the flora-bearing unit of the Ushi outlier is correlated with basal layers of this cycle.

On the whole, we should point out that the formation of quartzite-like sandstones in the described sections is characterized by two types of hydrothermal sources: (1) sources containing true silicic acid solutions leading to the formation of quartzites dominating in the Lob and Ushi outliers sections and (2) high-concentration varieties promoting the formation of siliceous gels and origination of sands with opal–chalcedony cement (the flora-bearing lens of the Ushi outlier).

The region described is located at the uplifted northwestern limb of the Transvolga flexure fault zone that was long developed in the uplifted northwestern peripheral region of the Caspian Depression in the Paleozoic, Mesozoic, and Cenozoic (Karta ..., 1978). They are located in the zone of the normal strike-slip

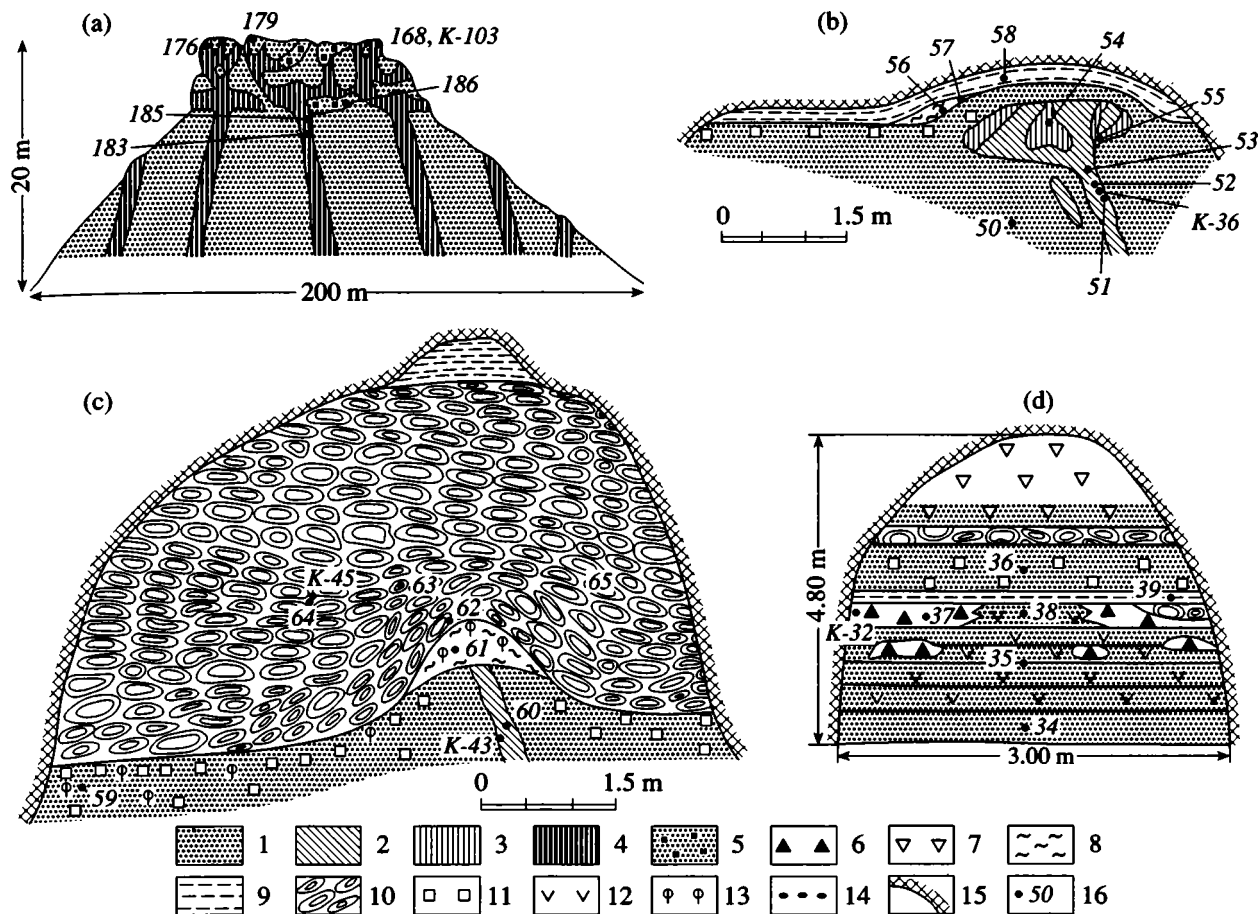


Fig. 4. (a) Idealized schematic structure of the Lob outlier near Kamyshin and (b–d) sketch of the exposures near the Lobachi farm. (1) Sands, (2) siliceous sandstones with opal veinlets, (3) opal with dispersed quartz grains, (4) quartzites, (5) quartzite-like sandstones, (6) cherts, (7) opokas, (8) halloysite clays, (9) smectite clays, (10) goethite iron ores, (11) ferrugination, (12) silicification, (13) phosphate segregations, (14) soil–plant cover, and (15) sampling sites and sample nos.

that extends from the northwest to the southeast approaching the Transvolga region and terminating near the Caspian Depression (Fig. 3).

The Don–Khopr interfluvial. The sections near the Lobachi farm (Figs. 4b–4d) are located at the eastern slope of the Voronezh anticline, in the upper gully at the Tishanka River right bank, 50 km to the southeast of Uryupinsk (Fig. 3). Here, the Senomanian sand unit (Sample 50) overlain by a wide range of the Khoper rocks (cherts, iron ores, and clays with a varying amount of macro- and micro-segregations of phosphates) is revealed in two exposures (Figs. 4b and 4c) at a distance of 15 m distant from each other. The bottom section of the Senomanian sands is destructured, pigmented by ferrous hydroxides, and includes secondary phosphate patches (Fig. 6, Sample 59a¹) filling a sand pore space and large voids in their upper destruc-

turized section. The decomposition of a sedimentation structure in the top section of the Senomanian sands is visible within 20–40 cm (sandstones with a destroyed structure, Fig. 4b, Sample 59).

In two points of the area under consideration (Fig. 4c, samples 51–53; Fig. 4b, Sample 60), the subvertical dikes, composed of siliceous material, crosscut the whole thickness (3 m) of the Senomanian sand exposure. In both cases, the dikes are represented by an opal mass (opal-CT) with patches of sandy material and separate sand grains (Fig. 6, Sample 52). The dike body has a nonuniform structure. It includes the alternating striated or tubular segments composed of more loose, white, substantially opal material, and dense, gray, more sand-enriched material. The fragments in Senomanian sands and transverse dikes have an identical composition (relative to the total amount of fragments): quartz (98%), feldspars (up to 2%), and glauconite (up to 3%). The chemical composition of rock samples from dikes and host sands is displayed in Table 2 (samples 50, 53, and 55).

¹ Here and further in the paper, the letters a, b, and c to the right of the rock sample number denote its individual mineral components that are separated in the form of patches, concretions, etc. (for example, the phosphate inclusion in sands (sample 59) is denoted as sample 59a).

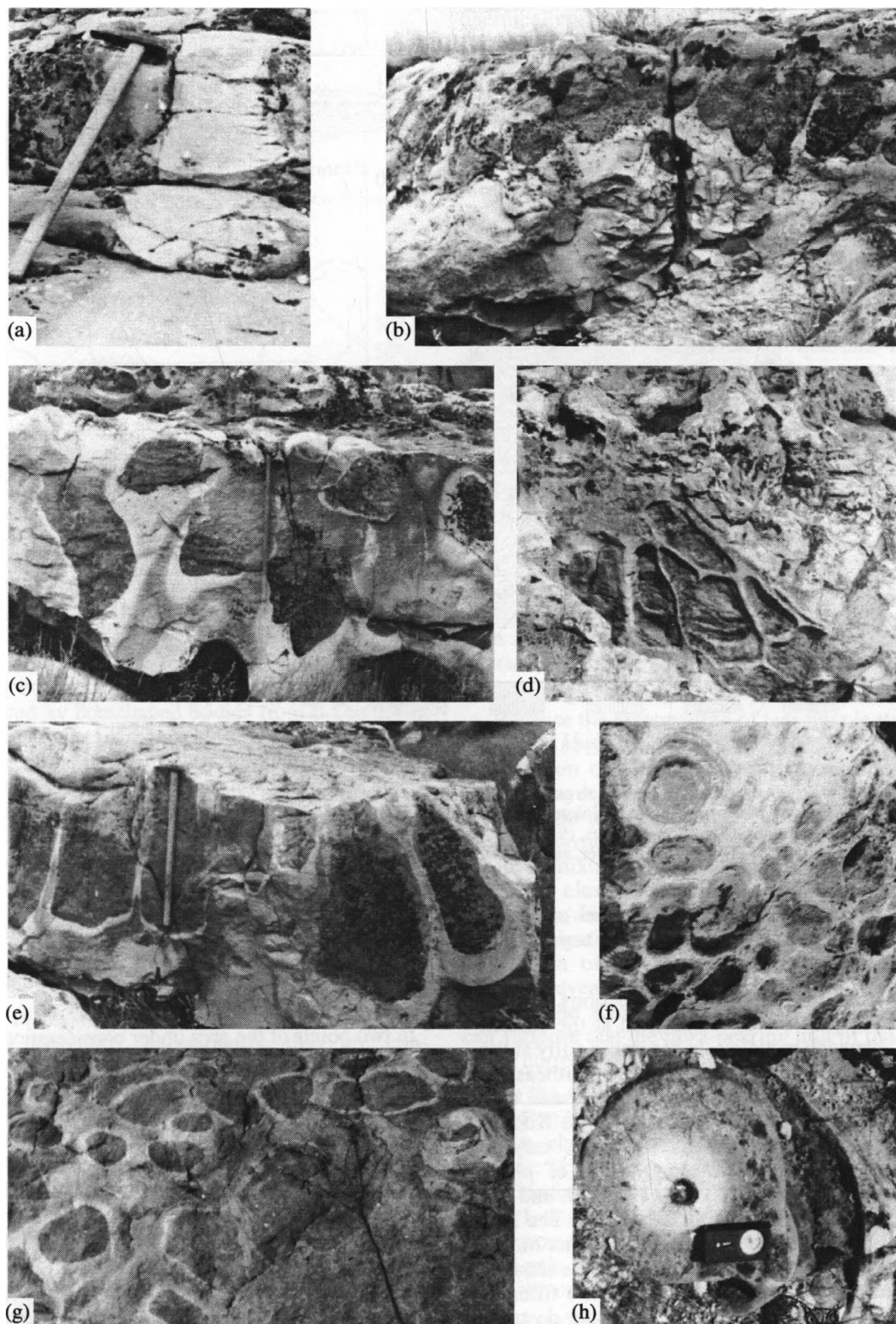


Fig. 5. Segregations and structures of the Kamyshin Formation sands transformed into quartzites (light spots in the photograph) with the remains of slightly silicified, semiloose, parent sands (dark spots in the photograph) in the Lob and Ushi outliers near Kamyshin: (a–e) in section, (f) in plan.

(a) Fragment of vertical siliceous dike in sands, (b–e) vein-striated quartzites, (f, g) tubular or circular-tubular quartzites, and (h) tubular quartzite with an open channel in the center.

Table 2. Chemical composition of rock samples (wt %)

Oxides	Sample nos.												
	50	53	55	60	56	61a	61b	62	63	58	G-33	183	185
SiO ₂	93.09	89.30	85.12	88.40	54.93	64.46	63.73	12.46	3.30	47.64	96.82	98.86	98.45
TiO ₂	0.38	0.44	0.17	0.13	0.10	0.26	0.26	0.26	0.61	0.71	0.47	0.13	0.09
Al ₂ O ₃	1.42	0.37	1.58	0.52	20.98	13.79	8.23	1.74	1.56	15.75	0.59	0.03	0.12
Fe ₂ O ₃	2.07	3.06	3.80	2.23	5.99	2.77	5.62	69.46	77.92	9.96	0.60	0.17	0.17
FeO	—	0.16	—	—	0.59	0.17	0.10	—	—	0.31	—	—	—
MnO	—	0.01	—	0.01	0.03	tr.	tr.	0.46	1.17	0.01	—	—	—
CaO	0.61	1.20	0.97	1.33	0.91	4.03	6.10	1.59	0.72	1.57	0.48	0.36	0.49
MgO	—	0.26	0.70	0.61	0.08	—	0.09	0.02	0.47	1.13	—	—	—
Na ₂ O	0.11	0.42	0.11	0.11	0.17	0.21	0.34	0.34	0.34	0.72	0.11	—	0.30
K ₂ O	0.31	0.37	0.15	0.12	0.14	0.23	0.33	0.17	0.25	1.10	0.21	0.05	0.07
P ₂ O ₅	0.04	0.03	0.66	0.68	0.46	2.56	4.10	1.21	0.35	0.15	—	—	—
L.O.I.	1.53	4.79	6.34	5.36	15.80	11.07	10.09	12.60	13.43	21.32	0.22	0.18	0.13
Total	99.56	100.41	99.60	99.50	100.18	99.55	99.65	100.31	100.12	100.37	99.50	99.78	99.82

Note: The sample reference to sections is shown in Fig. 4. The section near the Lobachi farm: (Sample 50) sands; (samples 53, 55, and 60) quartzite-like sandstones; (samples 56, 61a, and 61b) halloysite-containing clays; (samples 62 and 63) goethite iron ores; and (Sample 58) smectite clays. The sections near Kamyshin: (samples 183, and 185) quartzites (Lob outlier); (sample G-33) sands of the Kamyshin Formation, Balberka quarry. (—) Absent; (tr.) traces. Analyzed in the Analytical Center of GIN.

The dome-shaped bodies over dikes have different compositions. In outcrop I (Fig. 4c), the dome is composed of a colloform opal mass identified as opal-CT, with patches of sand and separate sand grains (Fig. 6, Sample 55).

Thus, the composition of a dike material is identical to that of a material in the bulge at the dike outlet. In both cases, the complete decomposition of the sedimentation structure of Senomanian sands, separation of clastic material, and consolidation of opal-sand masses are observed. The halloysite clay lenses (Fig. 6, Sample 56; Table 2) with the admixture of calcium sulfate semihydrate are observed along the bulge periphery. The ferruginous patches with viseite appear at the top of the halloysite clay section (Fig. 6, Sample 57b).² The Senomanian sands are overlain by bentonite clays (Fig. 6, Sample 58; Table 2).

At the outcrop II (Fig. 4b), one can observe a dike overlain at its outlet on the Senomanian sand surface by a complex dome including goethite iron ores with a coarse-block structure (Fig. 6, samples 62 and 63; Table 2). Each individual ore block is represented by a banded, Liesegang rings-type alternation of compact and relatively more loose ores. The lenses, gouges, and curved bands of mixed-layer smectite-hydromica clays are located between ore blocks (Fig. 6, Sample K-45). At the dome base, a lens of sandy halloysite clays (Sample 61) with block and microblock structure occurs immediately above the dike. The mineral com-

position of these blocks is considerably variable. Judging from the XRD and chemical analyses (Table 2, Sample 61a), quartz and halloysite are predominant in white patches of the sample; the francolite admixture is present as well. In yellow and brown patches (Sample 61b), the P₂O₅ content is increased up to 4.1% together with the increase in ferric iron (Table 2). Francolite and quartz are predominant in the individual rock blocks (Fig. 6, Sample 61c).

Outcrop III (Fig. 4d) is located 350 m west of the outlet area of transverse dikes. In this section, the stratified chert bodies (samples K-32 and 37) are present above the Senomanian destructurized, silicified, and ferruginous sands (samples 34, 35, and 38). They are represented by compact opal masses including numerous small shells of foraminifers replaced by silica. The chert structure is identical to that of a coccolite-foraminifer chalk (Fig. 2g). The chalk is evidently metasomatically replaced by opal. The structure of foraminifers is erased to a considerable extent, and it is impossible to identify their type affiliation. According to V.A. Krashenninnikov, the foraminifers resemble species widespread in lower stages of Upper Cretaceous, suggesting that the silica unit overlying Senomanian sands in section III apparently represent the Turonian chalk metasomatically replaced by opal. This assumption is supported by the occurrence of the Turonian chalk over the Senomanian sands within the study area (Don-Khoper interfluvial) in areas that are distant from transverse dike outlets and low-affected by metasomatism.

² Viseite is identified by reflections 5.68, 4.97, 3.48, 2.94, 1.888, 1.746, and 1.371 Å.

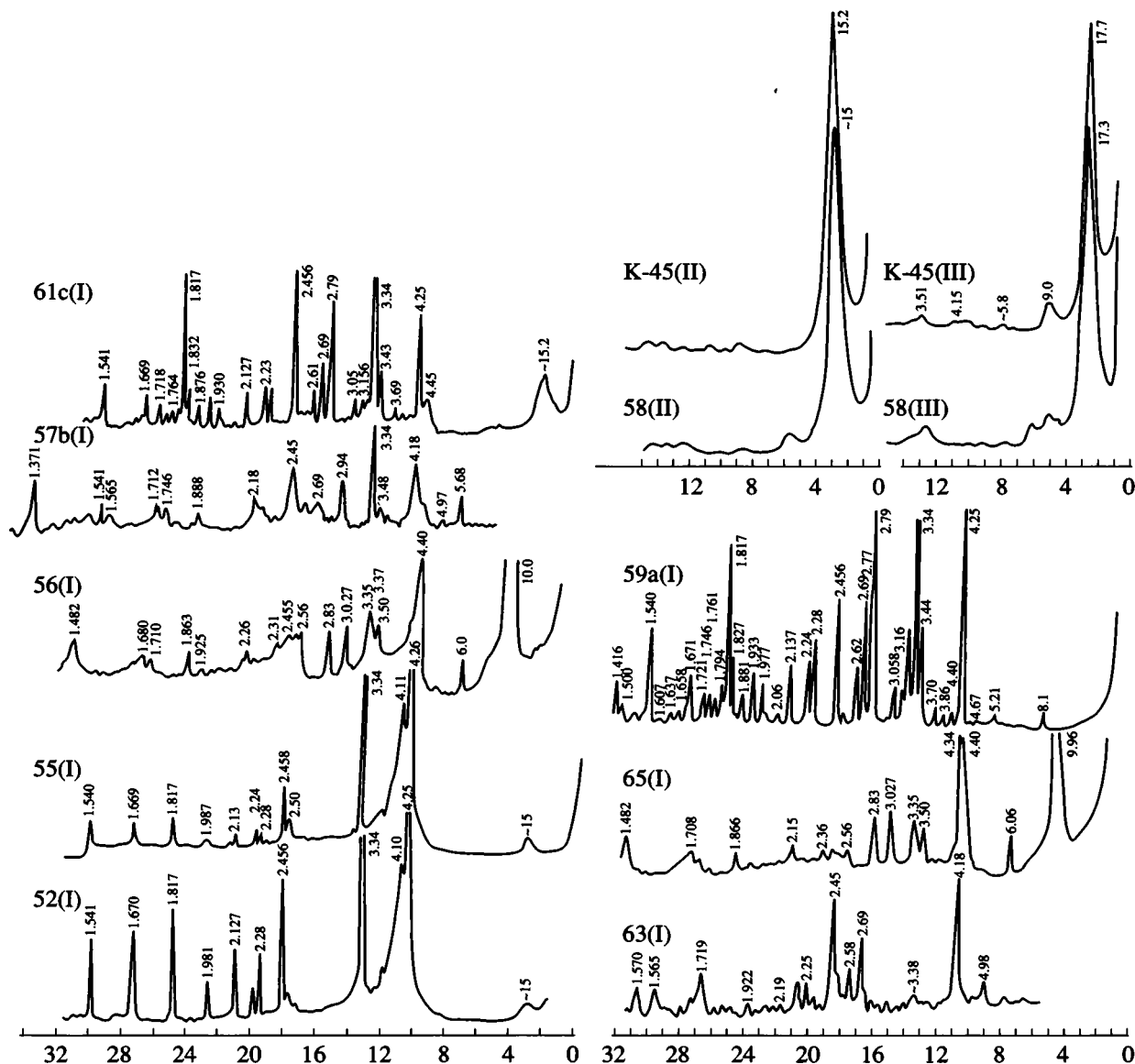


Fig. 6. XRD images of rocks samples from the Lobachi section: (I) powder sample, (II) natural sample oriented, and (III) oriented sample saturated with glycerin.

The sample reference is given in Figs. 4b and 4c (samples 52 and 55) quartz, opal-CT, and traces of smectite; (Sample 56) hydrated halloysite, semihydrate, and quartz; (Sample 57) viseite, goethite, quartz, and minor metahalloysite; (Sample 61c) apatite group mineral, quartz, and minor smectite; (Sample 63) goethite; (Sample 65) hydrated halloysite, semihydrate, and quartz; (Sample 59) quartz and phosphates; and (samples 58 and K-45) smectite.

Summing up the characteristics of siliceous (and ferruginous) rocks developed near the Lobachi farm, we point out their most important features.

(1) Dikes crosscut rocks underlying the Khoper Horizon and are genetically related to the stratified units of the Khoper rocks.

(2) Siliceous dikes and overlying bodies are composed of sand–opal rocks with a destroyed sedimentation texture. They are characterized by a new pulp texture, in which silica and ferrous hydroxides are the main rock-forming components.

(3) Chalk is metasomatically replaced by silica in the upper section of the pre-Khoper deposits.

It is of importance to point out that the studied ferruginous–siliceous deposits with phosphates, halloysite- and smectite-bearing clays, and other rocks in the Don–Khoper interfluvium (including the Lobachi farm district) belong to the Khoper stratum. Most geologists, complying with the conclusions of Askochenskii and Semenov (1973), assume that the Khoper Horizon represents the Lower Paleocene lateritic weathering crust of the Upper Cretaceous chalk–marl rocks partially

Table 3. Typification of the Paleogene quartzite-like sandstones of the East European Platform

	Type I	Type II
Morphology	Asymmetric, lenticular bodies with a flat top and irregular bottom	Lenticular, sheetlike bodies, usually symmetric, with subvertical branching bodies (dikes, veins) of quartzites
Location in the section of intraformation cycles	In the top of loose sand sequences below the layers of opokas, bentonites, or siliceous silts (clays)	Within sand sequences
Thickness	Up to 4–5 m	Up to 20–25 m
Internal layer structure, texture	Cementation decreases from top to bottom in a layer. Porous, filmy matrix	Uniform or nonuniform cementation within layers. Subvertical bodies are dike-shaped or complicated by tubular (circular) structures. Pulp textures may develop in dikes and layers. Filmy, porous, and regeneration matrix
Authigenic minerals of a matrix	Opal, lussatite, and chalcedony	Opal, lussatite, chalcedony, and quartz
Matrix origin	Diagenetic, epigenetic, or supergene due to sources related to post-sedimentation changes in overlying rocks	Hydrothermal (thermal water discharge)

redeposited in karst depressions and often additionally transformed by epigenetic sulfuric acid waters.

In this paper, disregarding the genesis of all the different-composition Khoper rocks developed over the considerable area of the Voronezh antecline and adjacent regions, we merely point out that the deposits near the Lobachi farm are not epigenetic eluvial formations. In their sections, the usual zonality of eluvial profile is not pronounced, and the upper dome sections are composed of smectite, whereas halloysite occurs in the lower, near-dike dome sections.

The morphology, structure, and mineral composition of rocks in dikes and overlying bodies testify to a deep-seated source of material supplied into solutions that are in extremely disequilibrium state under near-surface conditions, which has resulted in a geologically instantaneous disposal of large masses of siliceous gel, ferrous and aluminum hydroxides, and phosphates. In certain near-surface discharge areas of thermal waters, the top of Senomanian sands underwent uplift and folding followed by the sandy pulp injection into the apical part of dikes (exposure I).

Hydrothermalites under consideration, as well as stratal bodies, are free of faunal remains. Therefore, the find of foraminifer shells, replaced by opal, in the dike apex (Fig. 4c, Sample K-36) is of great interest. In this sample, V.A. Krashennnikov has determined the *Planorotalites pseudomenardii*, which is an index form of the Paleocene zone P-4. This points to the presence of marine conditions in the areas of thermal water discharge as well as makes it possible to date the period of hydrothermalite formation. The penetration of foraminifers from the upper layers is hardly possible because of geologically rapid lithification of siliceous gel and the presence of massive bentonite isolators at the objects under consideration.

Completing the characterization of the Khoper rocks near the Lobachi farm, it should be mentioned that at the eastern slope of the Voronezh antecline, a submeridional-oriented large graben restricted by the Losev–Mamon and Balashov faults is distinguished in the basement. In the graben's axial section, the Uryupin longitudinal fault (Fig. 3), regenerated in the Cenozoic, passes along lower reaches of the Khoper River (Karta ..., 1978). The considered hydrothermalites occur at one of the subsidiary normal faults on the west, and the strike of siliceous dikes coincides with the direction of normal fault, along which thermal waters might inflow.

CONCLUSION

The presented data on morphology, stratigraphic position, and matrix distribution within the rocks described testify to the existence of two types of layers of quartzite-like sandstones in the East European Platform. Table 3 displays their basic characteristics. The existence of two types of quartzite-like sandstones points to two fundamentally different mechanisms of their cementation or sources of free silica participating in their formation.

The Paleogene deposits of the East European Platform have a cyclic structure; the loose sand sequences occupy a well-defined position within the cyclic sections: they overlie biogenic nannoplanktonic sediments (marls and diatomites) or, when biogenic sediments are omitted, overlap opokas and glauconite sands composing the first element of cycles. In the complete cycles, sands are in turn overlain by basal unit rocks of a new cycle, i.e., by glauconite sands and opokas.

Thus, the asymmetric silicification of the top section of sands crowning the cycle is predetermined by the origination of overlying rocks capable of discharg-

ing considerable SiO_2 masses (bentonites and opokas) during diagenetic or epigenetic transformations. Within the sand sequence, the specific stratified sand levels may be silicified, and the symmetrical lenticular layers or dome-shaped bodies may originate due to either fundamentally different permeability of the specific layer or syn- or postsedimentary precipitation of amorphous silica that almost completely fills the sand pore space. Therefore, in the case of sandstones of the first type confined to the cycle top, it is evident that SiO_2 is supplied from the local source (the overlying bentonite or opoka layer), whereas in the case of the second type, we should suppose the existence of a fundamentally different, pulsating source, possibly connected with a hydrothermal inflow of material.

The type of authigenic silica (opal, quartz) can testify only to the degree of solution supersaturation with silica. The supersaturation of solutions due to increased temperatures or high alkalinity results in a rapid discharge of excessive SiO_2 in the form of gel, in which transformation continues for a million or even tens of millions of years (Mizutani, 1967) according to the scheme: opal-A–opal-CT(lussatite)–chalcedony (quartz). The SiO_2 precipitation from unsaturated solutions is regimented by the degree of supersaturation of true solution of H_4SiO_4 with respect to quartz whose solubility is no more than 8–10 mg/l (Wey and Siffert, 1961). Thus, the formation of quartzite-like mosaic structures due to the filling of primary pores with holocrystalline quartz may testify to the participation of siliceous true solutions, supersaturated only with quartz, in sand cementation.

The problem of the nature of ancient (deep layers, elisional, and juvenile) thermal waters requires special discussion.

Subsequently, one should pay more attention to the study of thermal water conduits and discharge areas for more complete solution of the problem of the role and scales of hydrothermal inflow of components into the Cenozoic platform cover. In this connection, the study of subvertical or ferruginous dikes and tubular bodies, often observed in the platform cover (Garetskii, 1956; Kaleda and Lipaeva, 1992) is of top-priority significance. The results of studies stated in this paper corroborate the conclusions of geologists (Kaleda and Lipaeva, 1992; Kholodov *et al.*, 1995) that, regardless of the nature (neptunic, injection, or autochthonous) of clastic material available in these dikes, the cementing matter is often of a hydrothermal origin.

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Zeolitization of Neogene Tuffs from Viet Nam

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Abstract—Zeolitic tuffs were first found within the continental part of Viet Nam. Their age is dated as Late Neogene. Zeolites (heulandite, phillipsite, chabazite, and erionite) replace basic volcanic glass and infill gas vesicles and other voids in ash-flow deposits and ash-fall tuffs. The zeolites are of a mixed “geoautoclave” and volcanogenic limnic genesis. Zeolites are transformed into bentonite under conditions of developed weathering crust and unstable tectonic settings.

THE PROBLEM STATEMENT AND INVESTIGATION HISTORY

The discovery of large commercial occurrences of natural zeolites in central and southern Asia (Transbaikalian region, Mongolia, Korea) and a theoretical substantiation of these discoveries allowed us to suggest a possible occurrence of genetically different zeolites in Viet Nam (Rasskazov *et al.*, 1991).

Geological settings in which different natural zeolites can appear and steadily exist were previously determined by many researchers. Summarizing these data, Senderov and Petrova (1990) distinguished three main types of such settings. The first type includes final stages of volcanic rock formation and associated pneumatolytic processes. This genetic type is named magmatic. Zeolites are crystallized in pore space of mainly amygdaloid basalts, especially if the lava effusion was on a water-covered surface. A diversity of zeolite mineral species is characteristic for such a type, but the first type has a commercial value only if thick and extended lava flows are zeolitized. Such settings are widespread in Viet Nam, and finding of zeolites in voids within amygdaloid rocks is quite probable.

The second type of setting is represented by hydrothermal metasomatic processes, where zeolites are formed due to reactions of circulating hot fracture water from various sources and immobile pore water with host rocks. This type can be expected in Viet Nam among facies of near-ore propylitic metamorphism. Laumontite and some high-siliceous zeolite varieties can be formed in such cases, being associated with epidote, chlorite, and albite.

The third lithogenetic type is the most widespread one. It includes all kinds of zeolite formation during the deposition and evolution of sedimentary and volcanic sedimentary rocks. Such a deposit type is commercially the most significant throughout the world. Among the

whole variety of diagenetic zeolitization processes zeolite formation during diagenesis of marine and lacustrine sediments is likely most widespread in Viet Nam. Necessary conditions for such zeolitization are a presence of reactive vitric ash particles or feldspars, and their interaction with slightly alkaline or alkaline paleolacustrine and paleomarine waters. The main zeolites formed are the following: clinoptilolite (in the case of slightly alkaline water), analcime, chabazite, erionite, phillipsite (in the case of alkaline water), and laumontite (at higher temperatures).

The mixed, hydrothermal diagenetic, zeolitization type was discovered on the oil-bearing South Viet Nam shelf in the early 1990s (Areshev *et al.*, 1992). The shelf rocks were studied in detail later by Shnip and co-authors (Dzjublo and Shnip, 1994; Pospelov and Shnip, 1995). According to the data by these authors, the zeolitized rocks were found during shelf drilling and prospecting for oil pools. Zeolitization zones are formed along tectonic or contraction deformations in granites, plagiogranites, and leucodiorites of the Jurassic–Cretaceous basement, and in overlying Oligocene sedimentary rocks, at depths of 3000 m and more. Zeolite (laumontite) partially or totally replaces plagioclase in primary rocks and infills fissures and other voids. It composes up to 30–40 vol %.

Pham Van Thuong, Professor of the Hanoi University, first began studies of zeolitization in the continental part of Viet Nam. He and his collaborators compiled two professional reports (1993 and 1995), where they described rare occurrences of laumontite, desmine, heulandite, and some other zeolites from weathering crusts on granites, basic volcanic and volcanic sedimentary rocks. Pham Van Thuong first suggested feasibility of the prospecting for zeolitic raw materials in Neogene volcanic sedimentary deposits within Viet Nam.

The materials presented in this paper were collected by us during field research in Viet Nam, in November–December 1995, performed according to the agreement

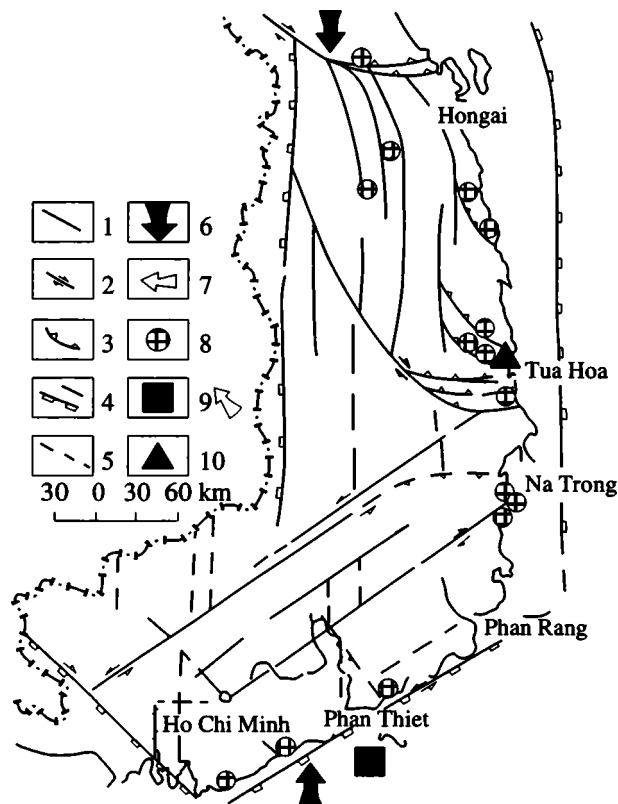


Fig. 1. Tectonic scheme of Viet Nam (Nguyen Trong Yem, 1991).

(1) Deep-seated faults; (2) horizontal strike-slip faults; (3) thrusts; (4) normal faults; (5) faults; (6) direction of recent compression; (7) direction of recent motion; (8) earthquake epicenters; (9) location of zeolitic (laumontitic) rocks on the shelf; (10) location of the Phu Luong section described in this paper.

on scientific co-operation between Russian Academy of Sciences and Viet Nam National Center of Natural Sciences. Field trips were held in eastern and southeastern parts of Viet Nam, where zeolite resources in volcanic and volcanic sedimentary rocks of the Jurassic to Quaternary age were revised, as well as those in Recent sediments from sodic mineral water springs. The zeolitization of Pliocene (N_2) basaltic tuffs and volcanic sedimentary rocks is described in this paper. Zeolites were formed and still exist not only in unstable tectonic settings characteristic for continent to ocean transition zones, but also in nonequilibrium conditions of mineralization within well developed weathering crust. These conditions, and a relatively young age of the zeolitization, determine the uniqueness of the zeolite occurrence described in this paper.

THE STUDY RESULTS

According to Nguen Trong Yem (1991), the central part of Viet Nam not only moved westward together

with the entire Indochina Massif, in Late Cenozoic, but also suffered a strong compression in the meridional direction (Fig. 1). These differently oriented stresses led to the origination of extension structures accompanied by intense volcanism, widespread in Viet Nam at that time. The continuous evolution of the volcanic products from picrites to tholeiitic basalts allowed Nguyen Xuan Han *et al.* (1991) to suggest magma sources to be at the depths of 60 to 40 km. Surface lava effusions were accompanied by explosive processes and by distribution of volcanoclastic materials over wide territories. Tephroids were accumulated in intermontane troughs, filled with isolated water basins during the Neogene. A sequence of vitroclastic basaltic tuff, containing heulandite, phillipsite, erionite, and chabazite, was discovered in one of such intermontane valleys near Phu Luong settlement, about 20 km northward of Tua Hoa city. Based on diatom remains, the age of this tuff, intercalated with bentonite and diatomite, is Late Neogene.

The zeolitized tuff occurs just near the foot of the volcanic edifice that produced them. It is impossible to determine the actual thickness of the section, owing to a thorough turfing of slopes, so we can only note that it is not less than 100 m. Lower parts of the section are exposed in a natural escarp up to 5 m high and are represented by typical pyroclastic flow deposits. As defined by Kraevaya (1977, p. 8): *Pyroclastic flows are mainly created by eruptions of highly explosive intermediate and acidic lava, representing at the moment of explosion a gas and liquid "emulsion" containing still ductile fragments of commonly pumicelike rock or pumice itself.* Just such a rock type is observed in the study area. Fiamme-like pumice inclusions and fragments of swelled pumicelike volcanic glass, immersed in psammitic and psephitic-psammitic tuff matrix, are well visible in the photograph (Fig. 2c). Moreover, rounded basaltic lava blocks, buried within fine-grained ash, are present in the lower part of the escarp described (Fig. 2b). This allows us to define the deposits as agglomerate tuff.

A brief description of rocks composing the section, and distribution patterns of authigenic minerals are given in Table 1.

In the lower part of the section, the pyroclastic flow tuff is characterized by psammitic, or more infrequently by psephitic-psammitic grain size and a light brown to almost white color; it is crosscut by a network of fine young fissures, partially infilled with calcite. The tuff is crystallo-, litho-, and vitroclastic in its petrographic composition. Crystal clasts and lithoclasts constitute about 5 vol %. They are included in a vitroclastic (now smectitized and zeolitized) matrix, composed of fine-grained sharp-edged basaltic glass fragments ($N = 1.580-1.587$); more than 90% of them are replaced by smectite, zeolites, amphibole, and an ore (Mn?) mineral. Crystal clasts (feldspars and less often, quartz) are unaltered. Fragments of trachybasalt and

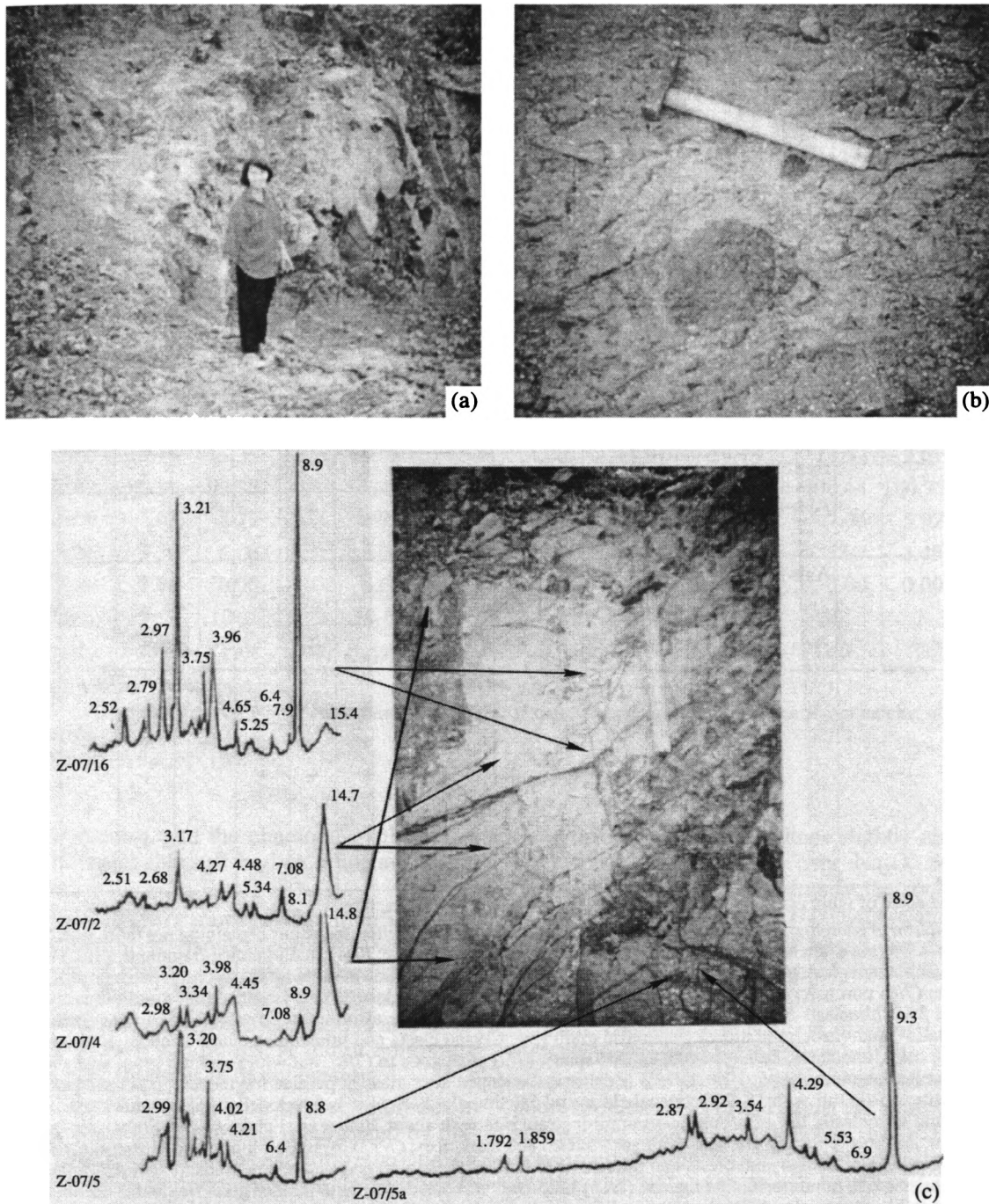


Fig. 2. Ash-flow tuff in the lower part of the Phu Luong outcrop. (a) General view; (b) inclusions of basalt fragments (dark) in psephitic-psammitic crystallo-, litho-, and vitroclastic tuff; (c) character of authigenic minerals distribution in the tuff. X-ray diffraction patterns: (Sample z-07/16) heulandite with minor smectite; (Sample z-07/2) smectite and phillipsite; (Sample z-07/4) smectite, heulandite, and phillipsite; (Sample z-07/5) heulandite; (Sample z-07/5a) heulandite and chabazite.

pumice occur among the lithoclasts. The pumice of andesitic basalt composition (containing glass with $N = 1.54-1.55$) is filled with gas vesicles and ore mineral dissemination. Large fiammelike pumice fragments have a similar composition. Agglomeratic fragments are composed of occasionally altered tholeiitic basalt.

An intercalation of tuffs, clays (bentonites?), and diatomites is observed upward the section (Table 1). The tuffs in the middle part are essentially similar to the counterparts in the lower part of the section, but sometimes differ in higher content (up to 20%, in some cases up to 40%) of crystal clasts and lithoclasts. The homo-

Table 1. Mineral composition of the rocks from Phu Luong section

Position in the section	Genetic rock type	Sample no.*	Authigenic minerals							Zeolite content, %
			Heulandite	Phillipsite	Erionite	Chabazite	Smectite	Calcite	Apatite	
Upper part, directly below basalt sheet	Ash-fall tuff with minor thin ash-flow interbeds	07/18	+				+			3–5
Middle part	Bentonite with diatoms	–/16b	+				+			3–5
	Ash-fall tuff with thin ash-flow interbeds	–/16a	+	+	+		+			25–30
	Diatomite	–/15	+				+			50–70
	Ash-fall tuff with thin ash-flow interbeds	–/14	+				+			<1
	Bentonite	–/13	+				+			1–3
	Ash-fall tuff	–/12		+			+			~30
		–/11	+				+			5–10
Lower part	Ash-flow tuff	–/10	+				+			1–3
		–/9		+			+			5–10
		–/8		+			+			5–10
		–/7					+			2–3
		–/6	+				+			20–30
		–/5	+			+	+			~10–15
		–/4	+	+	+		+			~50
		–/3						+		–
		–/2		+			+			~10
		–/1	+		+	+	+			~75

Note: The vertical scale of table is schematic. Apparent thickness is at least 100 m.

*Brief description of samples: (7/1) pumice. Zeolites infill gas vesicles; (7/2) vitroclastic tuff containing not more than 5% lithic clasts. Zeolites replacing glass are smectitized; (7/3) late fissure infilled with calcite; (7/4) small pumice fragments within litho- and vitroclastic tuff. Zeolites replace glass, and infill gas vesicles; (7/5) porous crystalline basalt with trachybasalt patches and zeolites infilling gas vesicles; (7/6) porous crystalline basalt with zeolites infilling gas vesicles; (7/7) crystallo-, litho-, and vitroclastic tuff (crystal clasts about 3%, lithoclasts 5%, and the rest is smectitized glass). Smectite also replaces zeolite of early generation; (7/8) porous litho-, crystallo-, and vitroclastic tuff of psammitic grain size. Crystal clasts and lithoclasts content is about 10%, and crystal clasts predominate over lithoclasts. Zeolites occur in free space; (7/9) analogous to (7/8), but with psephitic grain size and more porous; (7/10) bentonite containing about 10% clastics. Zeolite is developed after glass in pumice fragments; (7/11) psammitic litho-, crystallo-, and vitroclastic tuff with 15–20% crystal clasts and 5% lithoclasts. Zeolite is developed in intergranular spaces; (7/12) litho-, crystallo-, and vitroclastic tuff of psephitic-psammitic grain size with about 10% crystal clasts, 2–3% lithoclasts (mainly trachyte, rare pumice). Zeolites replacing glass occur in gas vesicles and interstices; (7/13) crystallo-, litho-, and vitroclastic tuff of psammitic grain size. Contents of both crystal clasts and lithoclasts is 20% each. Zeolite is developed in voids; (7/14) diatomite. Fragments of diatom frustules are in montmorillonite matrix; (7/15) litho- and vitroclastic tuff with pumice glass fragments. Zeolite replaces pumice glass and infills gas vesicles; (7/16a) crystallo-, litho-, and vitroclastic tuff of psephitic grain size. Zeolites replace glass and infill gas vesicles; (7/16b) bentonite with diatoms. Zeolites occur in micropore space; (7/18) litho- and vitroclastic tuff. Lithoclasts (up to 50%) are represented by coarse-crystalline basalt fragments. Zeolites occur in leaching voids plagioclase, and more rarely in gas vesicles.

geneous structure and the rather small thickness of individual tuff interbeds likely indicate their ash-fall origin. Variations in contents of crystal clasts, lithoclasts, and vitroclasts, and thus in the tuff composition, are possibly evidence of interruptions in the explosive activity and of different distances from volcanic centers producing the ash. Clay and diatomite interbeds even more emphasize this assumption.

The upper tuff bed, which underlies the thick tholeiitic basalt flow, distinctly differs from all other tuff beds in its petrographic composition. This is a crystallo- and lithoclastic tuff containing up to 60% or more crystal clasts and lithoclasts, and is composed of trachytic and pumicelike basalt fragments, plagioclase, and relics of dark-colored minerals. These components are immersed in dense glass matrix saturated with fine-dispersed ore mineral. Its

Table 2. Chemical composition of the rocks from Phu Luong section (wt %)

Oxides	07/1a	07/1a*	07/2	07/5	07/7	07/9	07/10	07/12	07/13	07/16a
SiO ₂	44.64	50.49	46.16	56.76	48.61	46.76	44.37	47.52	47.37	48.68
TiO ₂	0.65	0.73	1.62	1.01	1.58	1.52	2.38	1.50	2.77	1.93
Al ₂ O ₃	13.06	14.77	15.42	15.47	15.48	16.34	15.20	15.97	18.47	15.08
Fe ₂ O ₃	1.67	1.89	8.12	7.57	8.36	7.85	11.00	8.26	9.00	7.95
FeO	0.00	0.00	0.14	0.14	0.81	0.12	0.46	0.13	0.13	0.10
MnO	1.82	0.00	0.05	tr.	0.06	0.04	0.02	0.10	0.07	tr.
CaO	13.08	6.31	5.81	1.59	4.74	5.75	4.27	5.59	7.61	5.50
MgO	3.06	3.46	2.79	1.83	2.20	3.37	2.96	3.08	1.25	1.02
Na ₂ O	1.02	1.15	0.50	0.12	0.84	1.35	0.88	0.98	2.18	0.55
K ₂ O	1.81	2.04	1.78	0.74	0.84	3.52	0.31	2.59	1.31	0.69
P ₂ O ₅	1.51	0.00	2.01	0.03	1.46	1.92	0.70	1.40	0.98	0.88
L.O.I.	17.57	19.15	15.35	14.03	14.40	11.91	17.75	13.52	9.61	16.84
Total	99.89	99.99	99.75	99.29	99.65	100.45	100.30	100.64	100.75	99.22
H ₂ O ⁻	4.08	4.08	8.72	6.75	8.55	6.27	10.34	7.06	5.92	9.04
H ₂ O ⁺	5.36	5.36	6.08	6.70	5.52	5.44	6.92	5.97	3.45	6.58
CO ₂	7.50	7.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zeolites**	75	75	10	10–15	2–3	5–10	5–10	30	1–3	25–30
Rock	Pumice	Pumice	Tuff	Basalt fragment edge	Tuff	Tuff	Bentonite	Tuff	Tuff	Tuff

Note: (tr.) Traces. Analyst V.V. Karpushina.

*The analysis is adjusted to 100% after subtracting CO₂, Ca, P, F, and Mn consumed in the formation of calcite, apatite, and manganese oxide.

**Zeolite content in the rock (%).

position in the section, and the character of the clasts allows us to interpret this tuff bed as a hot avalanche deposit.

The major part (80% or more) of clay interbeds consists of dioctahedral ferrismectite matrix with rare, small fragments of quartz, feldspar, pumicelike glass, trachybasalt, and diatom frustules. The clay mineral is developed in volcanic glass fragments and is also crystallized in free growth conditions. A minor admixture of terrigenous clay minerals is likely present.

Diatomite interbeds are similar to clay interbeds in their structure, but organic remains represented by diatom frustules and sponge spicules and immersed in clay matrix predominate in their composition. In addition to clay, the inorganic material in these interbeds includes apatite, and minor amounts of feldspar and quartz fragments.

The chemical composition of rocks from the section is presented in Table 2. The analyses show that all varieties are intensely affected by secondary processes, as indicated by the loss on ignition values, which average about 14–15%. Such values are only possible if rocks contain much smectite or zeolite. Additionally, the rocks are characterized by high phosphorus content that is explained by a presence of authigenic apatite.

Primary composition of the tuff is characterized by a relatively low SiO₂ content (average about 47 wt %), and

by an average sum of alkalines slightly above 3%, with K₂O somewhat prevailing over Na₂O. Such chemical composition allows us to classify the rock as a normal basaltic tuff, with a high TiO₂ content (average 1.8%).

The marginal part of a basalt inclusion analysed (Sample 07/5) shows a composition close to andesitic basalt (SiO₂ content 56.76%).

Bulk chemical composition of altered pumice inclusions is represented by the Sample 07/1a. If we take into account that the pumice is now composed of 75% authigenic zeolite (Table 1) and adjust the analysis to 100% by subtracting excess components (Ca, CO₂, P₂O₅, F₂) consumed for the formation of secondary calcite and apatite, the SiO₂ content will be more than 50%. If the zeolite formation took place without any supplementary material input, then the aforesaid silica increase is an additional evidence for formation of the pumice inclusions from more acidic (andesitic basalt) derivatives of the initial magma.

High contents of P₂O₅ (19.91%) and CaO (22.00%) noted in diatomite (Sample 07/14) are related to a presence of apatite in the rock.

All rock types are zeolitized. Zeolites (heulandite, phillipsite, erionite, and chabazite) replace volcanic glass, or more rarely, feldspars and infill free pore space (Fig. 3). Their distribution in the rock is highly uneven. Figure 2c distinctly demonstrates that different types of

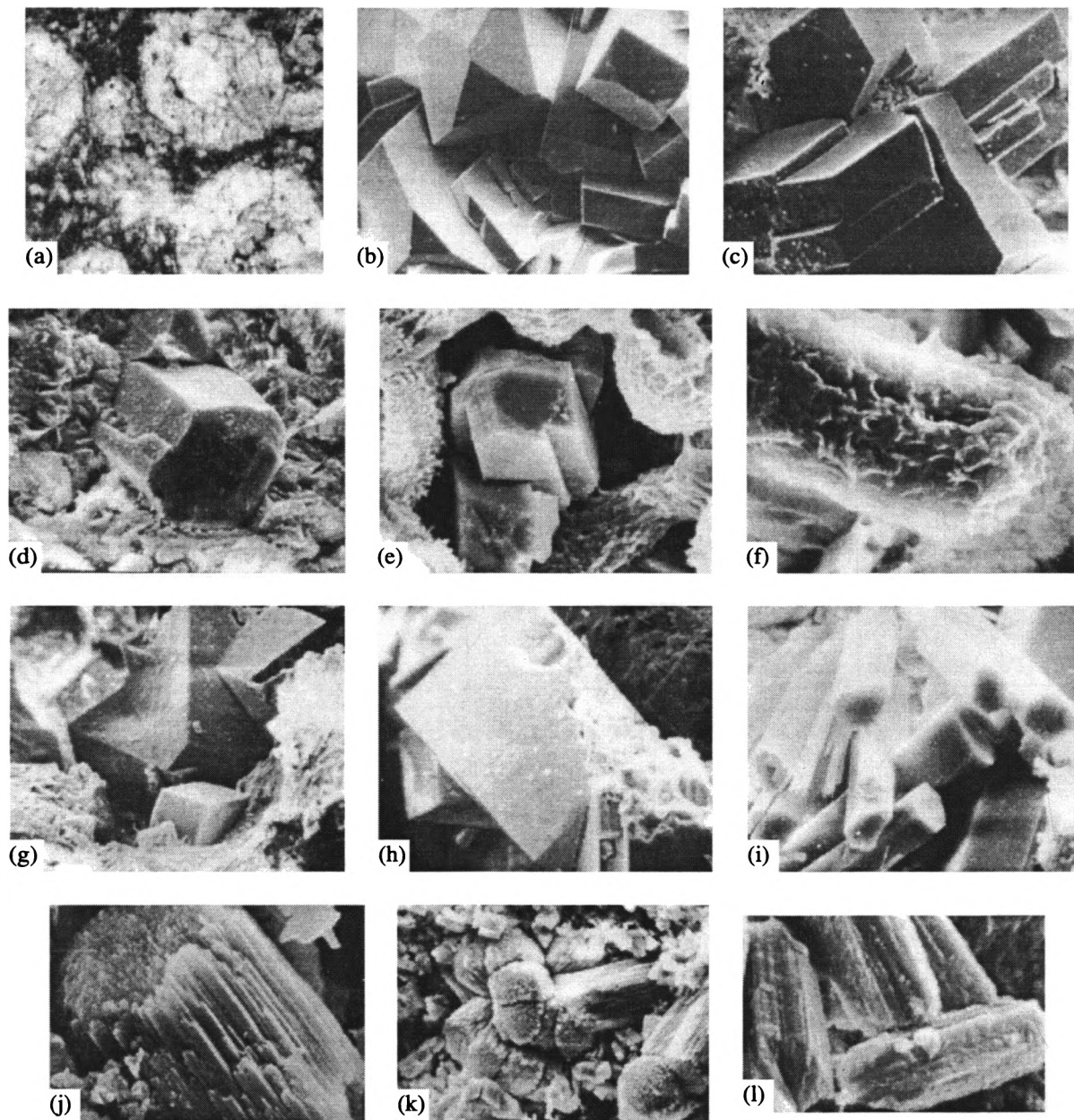


Fig. 3. Morphology of zeolites. (a) Heulandite and erionite in gas vesicles of pumice glass; (b) druse of heulandite crystals; (c) twin intergrowth of heulandite crystals; (d, e) prismatic phillipsite crystals in gas vesicles; (f) prismatic phillipsite crystals replaced by smectite; (g, h) morphology of chabazite crystals; (i–l) morphology of erionite crystals. Conditions of photomicrography: (a) optical microscope, transmitted light, magn. 200; (b–l) scanning electron microscope, magn.: (g, h) 500; (b) 1000; (c, d, e, i, k, l) 2000; (f) 5000; (j) 10000.

rock alteration can be found within a small (about 2 m²) outcrop area, as it is well reflected in X-ray diffraction patterns. Pumice fragments are the most altered. Heulandite, which commonly replaces the pumice fragments, may attain up to 75 vol %. Glass fragments in the dense vitroclastic tuff are commonly replaced by phillipsite. Chabazite occurs in zones with maximum amount of basalt fragments, and it often infills free voids in altered marginal zones of the basalt fragments. Erionite associates with all other zeolites, but occurs in

minor amounts. The erionite content increases up to 25–30% only in the upper part of the section, where it infills free space in porous tuff.

Zeolites are identified by their optical properties and X-ray patterns as follows.

Heulandite. Refraction index parameters $N_g = 1.490$; $N_p = 1.487$; and cN_g is up to 45°. X-ray diffraction patterns corresponding well to that of heulandite are shown in Figs. 2c and 4. Ignition at 200°C does not

Table 3. Interplanar distances (Å) of authigenic minerals from the Phu Luong section rocks

Heulandite 07/1		Phillipsite 07/2		Chabazite 07/5		Erionite 07/16a		Hydroxylapatite 07/14	
<i>I</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>
10	8.9	1	8.10	10	9.3	9	11.48	2	8.1
1	7.9	4	7.08	1	6.9	1	8.80	1	5.21
1	6.79	1	6.50	2	5.53	2	7.50	3	4.04
1	6.30	1	6.30	2	4.93	3	6.60	2	3.85
0.5	5.80	3	5.34	2	4.64	1	6.29	5	3.41
1	5.40	3	4.96	5	4.29	4	5.79	3	3.16
2	5.21	3	4.27	3w	3.95	1	5.41	3	3.06
2	5.27	4	4.09	4	3.54	1	4.57	10	2.79
3	5.10	1	3.66	1	3.43	10	4.33	6	2.69
4	4.69	1	3.43	1	3.21	1	4.21	4	2.62
2	4.35	4	3.21	2	3.14	3	3.81	2	2.51
6	3.95	6	3.17	3	2.98	7	3.75	2	2.28
5	3.89	4	3.14	4	2.92	4	3.58	4	2.24
4	3.74	2	2.93	4	2.87	1	3.40	1	2.21
1	3.56	1	2.73	1	2.48	2	3.32	1	2.12
4	3.41	3	2.68			2	3.30	1	2.05
2	3.31	3	2.56			4	3.18	1	2.02
6	3.21	3	2.51			1	3.15	1	1.934
4	3.17					1	3.12	3	1.932
3	3.12					1	2.95	2	1.879
1	3.04					4	2.88	3	1.834
7	2.97					4	2.85	2	1.792
1	2.81					2	2.81	2	1.765
4	2.79					2	2.68	2	1.746
3	2.73							2	1.720
1	2.68							1	1.633
3	2.52								

Note: The values are calculated from X-ray diffraction patterns of oriented specimens.

change the area and height of 020 peak with $d = 8.9$ Å. Further ignition at 350°C for 2 h leads to the appearance of "B phase" in the mineral, with $d = 8.3$ Å, and to the decrease in height and area of the peak with $d = 8.9$ Å. Both peaks totally disappear after ignition at 450°C for 2 h. Such thermal behavior of the mineral is characteristic for heulandite *sensu stricto*.

Morphology of heulandite is shown in Figs. 3a–3c. The crystal habit is not quite typical for heulandite. Crystal faces 011 are poorly developed, and the tops of crystals are flattened in some cases. The tops of some crystals represent tetragonal pyramids. Rare twins also occur (Fig. 3c).

The chemical composition of the mineral has not been studied to date. However, if we subtract contents

of CO₂, MnO, P₂O₅, F₂, and part of CaO and Fe₂O₃, consumed for the formation of calcite, apatite, and hydroxides of Fe and Mn (Table 2), then we can assume that the residue of the pumice analysis would be close to the proper heulandite composition, as the pumice consists of 75% heulandite. Heulandite is likely represented by its Ca–Mg variety, in which the alkali (K₂O + Na₂O) content is subordinate and K₂O slightly prevails over Na₂O.

Phillipsite. As indicated from the X-ray pattern (Fig. 2c), interplanar distances of our phillipsite completely coincide with standard ones (Table 3). The morphology of phillipsite crystals is shown in Figs. 3d–3f. Elongated phillipsite crystals rarely display distinct crystallographic habit (Figs. 3d, 3e). Their edges are pseudorounded, and the crystals themselves are

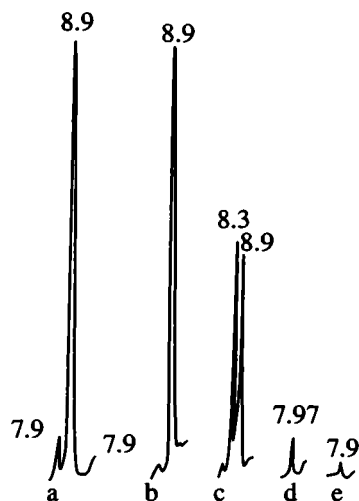


Fig. 4. Fragments of X-ray patterns of heulandite. Oriented specimen: (a) natural state; (b–e) ignited during 2 h at temperatures (°C): (b) 200; (c) 350; (d) 450; (e) 550.

replaced by smectite (Fig. 3f) that complicates the mineral identification. Phillipsite is almost isotropic, and its

refraction index is about 1.490.

Chabazite is represented by pseudocubic crystals (Figs. 3g and 3h), with $N_c = 1.475$ – 1.476 ; $N_o = 1.472$ – 1.473 . X-ray diffraction pattern is shown in Fig. 2c, and interplanar distances are given in Table 3.

Erionite is represented by sheaf-like aggregates of fine acicular crystals, or by individual hexahedral prismatic crystals (Figs. 3i–3m). It is almost isotropic, with $N \sim 1.483$ – 1.484 . Its d values are given in Table 3.

Besides zeolites, **smectite** is a major secondary mineral in all tuff varieties. X-ray diffraction patterns of its natural specimens display 001 reflection within the limits 14.7–15.4 Å, and in glycerine-saturated specimens the reflection is shifted to 18.0–18.6 Å. Reflection 060 is 1.520 Å. Such X-ray diffraction parameters correspond to both dioctahedral and trioctahedral smectites. Chemical composition of the rock, composed of mostly (more than 90 vol %) smectite, is given in Table 1 (Sample 07/10). The analysis, adjusted to smectite formula, corresponds to:



i.e., it corresponds to high-Fe montmorillonite. Hence, dioctahedral high-Fe smectite is likely present in the sequence.

Apatite is another stable secondary mineral. Judging by P_2O_5 content (Table 1), apatite occurs in all the rock types composing the section, but its highest contents are found in diatomite. The apatite formation is possibly a result of large-scale fauna and flora dying owing to burial under thick volcanic ash cover. Phosphorus released from organic matter during the burial can interact with volcanic gases (particularly with F_2 and CO_2), and with Ca extracted from surrounding rocks. The d values of apatite shown in Table 3 correspond to those of standard hydroxylapatite.

Abundant precipitates of X-ray amorphous Mn-mineral are often noted at final stages of the tuff alteration. The manganese mineralization is abundant during alteration of pumicelike glass fragments, as it is well demonstrated by both altered tuff photographs (Fig. 2) and chemical analyses (Table 2, Sample 07/1a).

DISCUSSION

The presence, in the rocks studied, of numerous diatoms of the family *Melosiraceae* (*M. praegratulata*, *M. praegratulata* var. *muzzanensis*, *M. praeislandica*, etc.), which are habitants of large freshwater or slightly saline lakes, indicates that the ash was deposited in water basins. As it follows from the above description, the zeolite-bearing sequence is composed of basaltic tuffs of different genetic types. The lower part of the

section is represented by ash-flow deposits which presuppose increased thermal characteristics and high vapor and gas contents of the ash during its consolidation. The middle and upper parts of the section are composed of intercalated tuffs, bentonites, and diatomites. A minor proportion of the tuff beds is represented here by ash-flow deposits, similar to those described, but thinner, whereas a majority of the beds is deposited from ash-falls, also characterized by rather high temperatures. The entire sequence is overlain by a thick basaltic lava sheet that served as a low-permeable thermal screen. The abundance of available lake water, high temperature, and gas saturation of volcanoclastics in the sequence create favorable conditions for the authigenic mineralization. Later minerals, including zeolites, are crystallized from solutions formed by interaction of cold water with still warm volcanic material.

This kind of zeolite formation was defined as geoauto-clave mechanism by Alexeev and Djiurova (1975). A wide range of temperatures and chemical compositions of solutions leads to the formation of practically all known zeolites in a free space within volcanic rocks. As a rule, this type is characterized by crystallization of zeolites directly from solutions, with a minor participation of metasomatic processes. The geode-hosting rock is somewhat altered only in rare cases: even such unstable minerals as olivine, plagioclase, and orthopyroxene are unaltered. Alexeev and Djiurova (1975) applied this model to the formation of clinoptilolitic ash from northeastern Rhodopes, and Lenzi and Passagli (1974) used it for chabazitic tuffs from Italy.

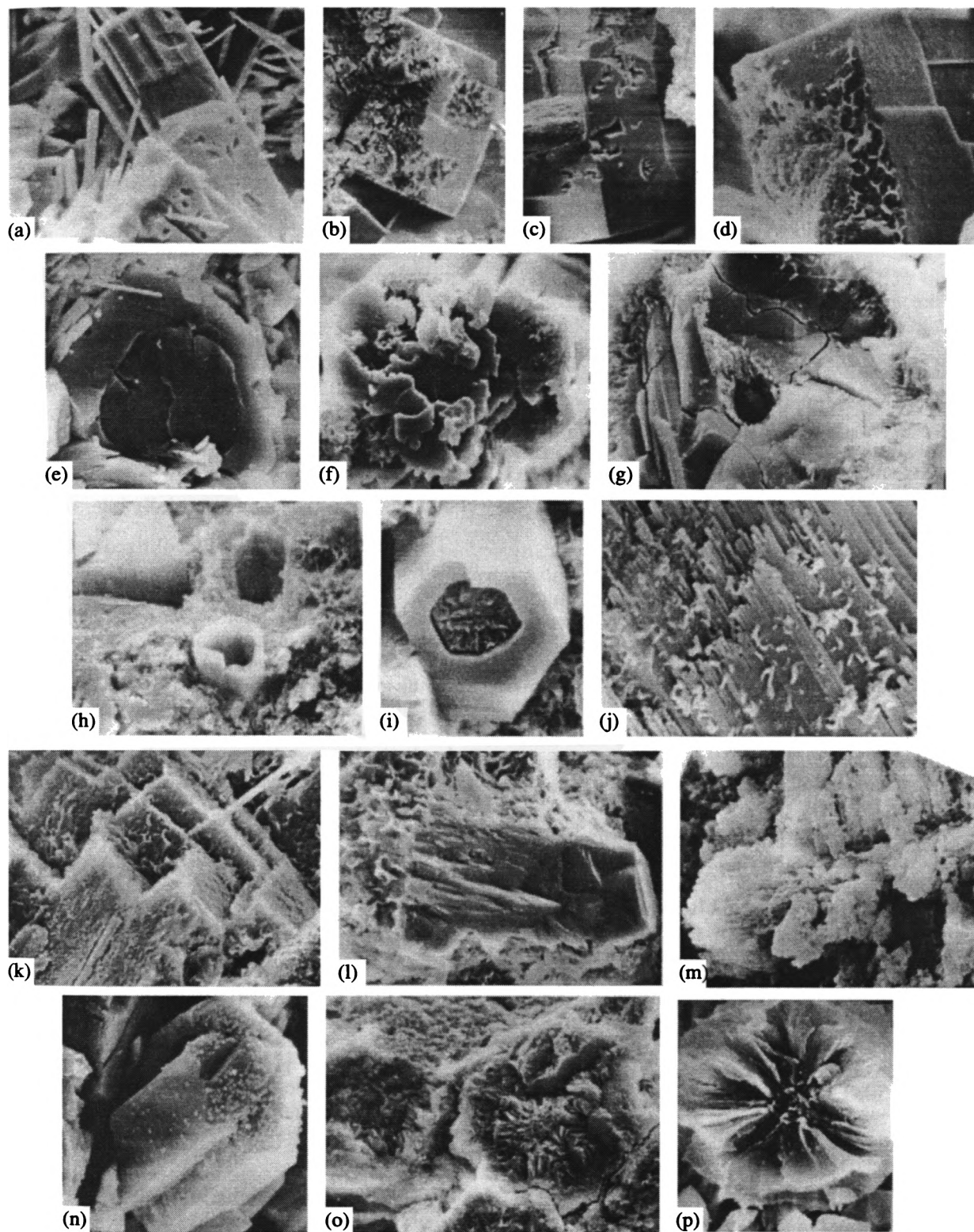


Fig. 5. Dissolution and replacement of zeolites. (a) Erionite; dissolution figures on crystal faces and fine acicular crystals of second generation; (b) chabazite; partially dissolved and replaced by smectite; (c) heulandite; dissolution figures on crystal faces; (d) philipsite; partially replaced by smectite; erionite: (e) encrusting primary zeolite (phillipsite ?), (h) developed as rim and associated with primary zeolite leached off from the center, (i) with the leached center infilled with smectite, (f) dissolution of a large crystal; (g) dissolution of a large crystal and replacement by smectite; (j) initial replacement stage of fine acicular aggregate by smectite; transformation stages of: (k, l, n) phillipsite crystals into (m, o, p) clay aggregates. Conditions of photomicrography: scanning electron microscope; magn.: (c, d, o) 1000; (a, b, k, l) 2000; (e, f, g, h, m, n) 5000; (i, j, p) 10000.

A similar mechanism is also applicable to the zeolite associations described here. Porous pumice fragments in the tuff, which were the hottest and the most saturated by gases, and possibly swelled at the moment of their deposition, are most intensely zeolitized (up to 75%). All voids in these fragments are filled with well-formed heulandite and erionite crystals. Interstices in porous basalt fragments captured by ash-flows are filled with chabazite crystals.

However, the zeolitization also bears features of a volcanogenic-limnic origin. Zeolites, in tuff varieties composed of fine, cemented flyer-shaped glass fragments, are crystallized by means of metasomatic replacement of glass and of other reactive rock components. As a glass of basaltic composition is replaced, a low-siliceous zeolite (phillipsite) is formed in this case.

The paragenetic mineral association zeolites + smectites is most characteristic for all known zeolite occurrences in the world. Interrelations between zeolites and smectites show that these minerals are commonly formed either simultaneously, or successively, but within a single mineralization event.

Zeolites, commonly phillipsite, are typically replaced by smectite in these zeolite rocks. Details of this process are well visible in the series of photomicrographs (Fig. 5), where a later formation of smectite relative to zeolite is obvious. Zeolites may be replaced either partially or totally (Figs. 5n, 5p, and 5r). This allows us to suggest that amounts of zeolites (especially of phillipsite) is now considerably lower than it was at the moment of their formation, and that the later alteration is likely related to a transformation of tuffs under changed physical and chemical conditions of mineral formation.

Changing mineralization conditions during a lifetime of zeolites are also inferred from the fact that erionite, the zeolite with highest magnesium content, is commonly crystallized last of all. It forms late acicular generations (Fig. 5a), or "encrusts" zeolites of earlier generations, as well shown in Fig. 5e. Zeolite constituting the central part of a crystal becomes unstable with time and under changed environmental conditions and is leached. Instead of the primary zeolite (phillipsite?) + erionite association, only skeletal erionite crystals remain (Fig. 5h), where hollow central parts are infilled with smectite (Fig. 5i). Therefore, we can suppose that solutions became more alkaline, and magnesium content increased during the evolution of mineralization environments. These changes were likely related to drying up of the basins where ash sequences were deposited earlier. The drying up was possibly caused by changes in a general tectonic setting within the territory.

The influence of weathering agents on the postsedimentary transformations of zeolites was likely very strong. The early stages of weathering are commonly characterized by circulation of acid mineralizing solutions in the rocks. These solutions are aggressive relative to zeolites, residual volcanic glass, and other pri-

mary and secondary components of an altered tuff (including smectite). They dissolve the tuff, and leach off considerable amounts of cations. Traces of zeolite dissolution, as well as zeolite replacement by late smectites, are permanently present (Figs. 5a, 5b, 5f, etc.). Today, we are perhaps unable to distinguish first generations of smectite, synchronous to zeolites. Therefore, in conditions of developed weathering crust, we observe a continuous process of authigenic mineral formation. This process is developing on the basis of an already altered rock, due to reworking not only of its primary constituents, but also of secondary ones, such as zeolites.

High content of bivalent iron, widespread development of montmorillonite, presence of authigenic apatite, and dissolution of siliceous diatom frustules, now observed in the tuff, indicate that the present-day authigenic mineralization takes place in alkaline conditions. It is manifested not only by prevailing smectitization, but also by formation of actinolite and new generations of zeolites, the latter being especially interesting.

Therefore, the previously zeolitized tuffs become unstable under conditions of the hot tropical climate, and are more or less transformed into clay or clayey-zeolitic rocks. The thinner are primary tuff beds, the more intense is this process. Initially zeolitized ash-fall tuff sequences are widespread within a radius of 10 km from the outcrop described and are now completely transformed into bentonites, with zeolite content not more than 1–3%. These bentonites may have important technological properties, such as high sorption capacity, in particular. However, this problem needs additional investigation.

CONCLUSION

Zeolitized tuffaceous rocks with a high (up to 75%) zeolite content were first discovered within the continental part of Viet Nam. Based on diatom remains, the age of zeolite-bearing deposits is dated as Late Neogene. Zeolites, represented by heulandite, phillipsite, chabazite, and erionite, replace basic volcanic glass, and infill gas vesicles and other voids in ash-flow and ash-fall deposits. The zeolites have the mixed "geoautoclave" and volcanogenic-limnic genesis, and their composition depends on primary composition and structure of the tuff.

Zeolites, commonly rather stable in surface zones of lithogenesis, become metastable under conditions of a developed weathering crust and unstable tectonic settings related to different stages of rifting and are replaced by more stable late generations of smectite, and, more rarely, by new zeolites of other composition. The transformation of rocks, already altered into zeolite, may be so active that zeolitized tuffs will be replaced by bentonites.

ACKNOWLEDGMENTS

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Ore Occurrences in Effusive Siliceous Oceanic Complexes of the Koryak Highland

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Abstract—Different types of ore occurrences, which are encountered in the oceanic terranes of the Koryak Highland, are considered. These are hydrothermal sulfide, hydrothermal sedimentary Mn-bearing, and ferruginous metalliferous deposits of two types: basal Mn-free crusts and intraformational deposits with manganese admixture. A comparison is made between the similar ore occurrences in the Pacific Ocean and those developed in ophiolites of Cyprus and Oman. The accumulation of Santonian–Campanian intraformational metalliferous deposits probably reflects tectonic activation of the oceanic floor at that stage of the Pacific evolution and is caused by a hydrothermal activity within a Late Cretaceous spreading zone separating the Kula Plate from the Vaamychgyn Plate. Fragments of the latter were incorporated in the accretionary structure of the Koryak–Kamchatka rim of the Asian continent.

Effusive siliceous complexes are typical of orogenic belts and have long since attracted the attention of researchers of diverse geosciences: tectonicists, petrographers, lithologists, and ore geologists. A great body of information concerning these complexes and their metallogeny was summarized at the beginning of the 1950s once the study of formations became the principal method of elucidating the evolution of geosynclinal zones in the USSR. The main aspects of the formational approach were discussed by Shatskii (1954) and Kheraskov (1951, 1958). A series of collected works *Regularities in the Distribution of Mineral Resources*, in which the problems of metallogeny are considered from this standpoint, were published.

The success in studying the geology of modern oceans and the development of a theory of lithospheric plate tectonics, according to which ophiolite complexes of eugeosynclinal zones, including also effusive siliceous deposits, represent relics of former oceans, provided opportunities to use a comparative lithological method for the clarification of a genetic essence of the paragenetic associations established in geosynclinal formations and for the understanding of their metallogeny. Many small ore deposits and ore occurrences related to effusive siliceous complexes of orogenic belts, which are not of great economic importance and are often used for domestic needs, became the objects of detailed investigations for paleogeodynamic reconstructions. For example, low-grade iron ore found at the base of sedimentary cover of the Troodos Ophiolite Massif in Cyprus and the Semail Nappe, Oman, and used as a raw material for making a mineral paint (umber) attracted the attention of many researchers by its similarity to some types of metalliferous sediments from the southeastern Pacific Ocean. This similarity stimulated the detailed petrogeochemical study of the

Cyprus and Oman umbers and their comparison with oceanic metalliferous accumulations started by Robertson with his colleagues (Fleet and Robertson, 1980; Kaleda and Krylov, 1992; Robertson and Fleet, 1980; Robertson and Hudson, 1973).

The discovery of geothermal fields with a discharge of high-temperature hydrothermal solutions (known as “black and white smokers”) on mid-ocean ridges and within intraoceanic island-arc systems allowed us to define more precisely and sometimes to revise the idea of the origin of many massive sulfide ore deposits. The similarity between hydrothermal sedimentary accumulations within the zones of “black smokers” activity and Silurian–Devonian massive sulfide ore deposits in the South Ural was shown in a conclusive way. First of all, it is proved by the similarity of the ecosystems, in which recent and ancient sulfide ores accumulated on the seafloor (Maslennikov *et al.*, 1995). They are distinguished as ecosystems including organisms (large gastropods, some genera of bivalve, giant vestimentifera, worms, sometimes sea cucumbers, deep-water shrimps, crabs, and eels) whose nourishment is based on chemosynthesis owing to the bacterial use of hydrogen sulfide or methane.

Structure and mineralogical composition of the well-studied ore-bearing mounds in the Galapagos Rift Zone admitted of explanation of many regularities in the distribution of ore components in manganese ore deposits developed in Mesozoic effusive siliceous sequences in orogenic belts of the eastern margin of the Pacific Ocean. They include the ore manifestations in Campanian deposits of the Nicoya Ophiolite Complex in Central America (Kuypers and Denyer, 1979) and in Jurassic deposits of the Franciscan Formation of California (Grigor'ev, 1984; Sokolova, 1982).

The paper deals with the results of study of ore occurrences found in oceanic terranes of the Koryak Highland as compared with the metalliferous sediments of the Pacific Ocean and other regions of its structural framework, as well as with the ore-bearing accumulations in the similar deposits of the central Mesotethys, which are similar in age and formational composition. The work was mainly done on the basis of original data that we collected together with our colleagues in GIN during the investigations in different areas of the Koryak–Kamchatka orogenic belt. Up till now the metallogeny of its geological complexes has not been specially considered, although in some papers sulfide ore occurrences and the findings of Mn- and Fe-bearing rocks were noted. We think that the specific metallogeny of the oceans (including that related to hydrothermal discharge) can be viewed as one of the manifestations of the peculiarities of oceanic-type lithogenesis distinguished by Strakhov (1976b) and recently revised by Khvorova (1994, 1995a, b). Data on the metallogeny of accreted oceanic complexes contain important information on the paleogeodynamic position of the studied oceanic terranes and for the facies analysis of the related deposits.

RESULTS AND DISCUSSION

The oceanic terranes revealed within the Koryak Highland are shown in Fig. 1. The completeness of their sequences, age, and position in the modern structure of the Koryak Highland are different. The related problems were touched on by us and our colleagues in a number of previous papers (Grigor'ev *et al.*, 1994; Ruzhentsev *et al.*, 1982). In this paper, the iron and manganese ore occurrences in the Kuyul, Mainitsa, and Yanranai terranes are scrutinized.

Kuyul Ophiolite Terrane. A comprehensive study of the Kuyul Terrane carried out by geologists of GIN and the Far East Geological Institute (Far East Branch, Russian Academy of Sciences) with the involvement of some specialists of other organizations revealed a complex imbricate-folded structure of this terrane. It was proposed to use this terrane as an example of distinctive accretional type of structured serpentinite melange, in which the typical of melange chaotic distribution of clasts is combined with some regularity in their composition (Sokolov *et al.*, 1996). This regularity is displayed in that each slab (sheet) of melange differs from others by the compositions of certain sequence fragments and smaller clasts included in serpentinite matrix (Fig. 2). Various-size blocks of Upper Triassic–Jurassic oceanic deposits, assigned to the Kingiveem Formation, predominate in most of the slabs of the Kuyul Terrane. They differ from each other by their facies type, paleogeodynamic affiliation, and radiolarian remain assemblages (Grigor'ev *et al.*, 1995; Pral'nikova and Vishnevskaya, 1996). Mineral and geochemical differences of peridotitic relics from discrete slabs were also noted. The Udachnaya slab (lowermost among the tec-

tonic slabs in the Kuyul Terrane) and the Gankuvayam slab (second from the top) especially stand out because of the composition of rock fragments. The Udachnaya slab differs from all others by the predominance of fragments of metamorphosed rocks altered to green schist facies, which seem to have formed from rocks of the Kingiveem Formation. In the Gankuvayam slab, the only well-preserved, sulfide ore-bearing ophiolite section within the terrane is exposed. This section is most completely exposed in the Gankuvayam River valley. It represents the full range of ophiolite succession, from harzburgite to pillow lava flows (*Kuyul'skii ...*, 1990). Beyond the ophiolite section, a peculiar kind of low-titanium basaltoids of boninite affinity is related to the same slab.

Most researchers believed that the Gankuvayam ophiolites underlie all effusive siliceous deposits of the Kingiveem Formation found in other slabs of the Kuyul melange. However, now, on the basis of the findings of radiolarian remnants in rare siliceous lenses among lava pillows, as well as radiometric datings, it is established that the age of the Gankuvayam effusives is the Middle–Late Jurassic (Krylov *et al.*, 1995; Sokolov *et al.*, 1996). Hence, the Gankuvayam ophiolite could in no way be a paleoceanic floor for the Upper Triassic–Jurassic Kingiveem sequences.

Sokolov *et al.* (1996) suggested that fragments of other, more ancient ophiolite sections, which were destroyed in the course of accretion, are present in the composition of other slabs of the melange. Recently, some data appeared that indicate the probable presence of the relics of older oceanic crust in the Gankuvayam slab as well. For instance, the study of remanent magnetization in the effusive dike part of the Gankuvayam ophiolite section showed the presence of samples with both relatively low-latitude and high-latitude inclinations. In our opinion, it is reasonable to consider the first of them as the relics of older oceanic crust formed in the more southern latitudes (Krylov *et al.*, 1995). The presence in the effusive dike part of two kinds of basaltoids—typical oceanic tholeiitic (relic) rocks and differentiated calc-alkali (younger, proper Gankuvayam) rocks—agrees well with the data on the different magnetization of the rocks. The geochemical peculiarities of the Gankuvayam plagiogranites and the differentiated series rocks allow the Gankuvayam ophiolites to be attributed to suprasubduction complexes in much the same way as ophiolites of the Troodos Massif and the Semail Nappe (Luchitskaya, 1993; Krylov *et al.*, 1995; Sokolov *et al.*, 1996).

Sulfide mineralization of the Gankuvayam slab, as in ophiolites of the Troodos Massif, tends to be concentrated at the boundary of the complex of parallel dikes and effusives (*Kuyul'skii ...*, 1990; Chudaev *et al.*, 1993). The Gankuvayam ore occurrence has a vein form and is represented mainly by pyrite and chalcopyrite. According to Chudaev *et al.* (1993), the content of Co and Zn in pyrites is insignificant (about 0.05%); the

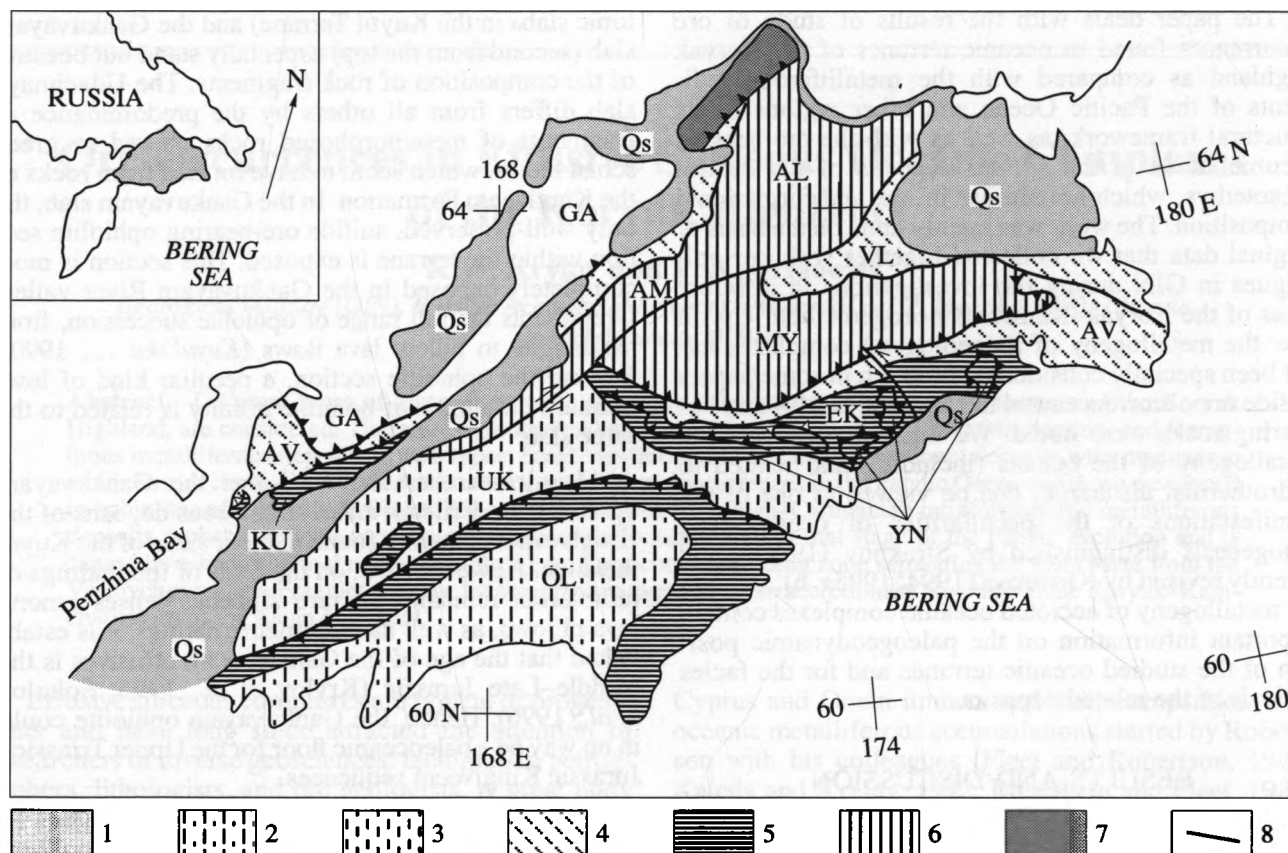


Fig. 1. Location scheme of Mesozoic oceanic terranes in the Koryak Highland. (1) Neogene-Quaternary deposits of superimposed basins; (2) Cenozoic island-arc complexes; (3) Cretaceous-Paleogene terrigenous deposits; (4) Cretaceous terrigenous deposits of fore-arc complexes; (5) Mesozoic oceanic terranes; (6) Mesozoic terrigenous deposits of back-arc basins and marginal seas; (7) Paleozoic deposits, undifferentiated; (8) faults and boundaries of terranes. Terranes: (OL) Olyutor, (YN) Yanranai, (EK) Ekonai, (KU) Kuyul, (AM) Ainyn, (GA) Penzhina-Anadyr, (AL) Algan, (VL) Velikorechinsk, (MY) Mainitsa, (AV) Alkatvaam.

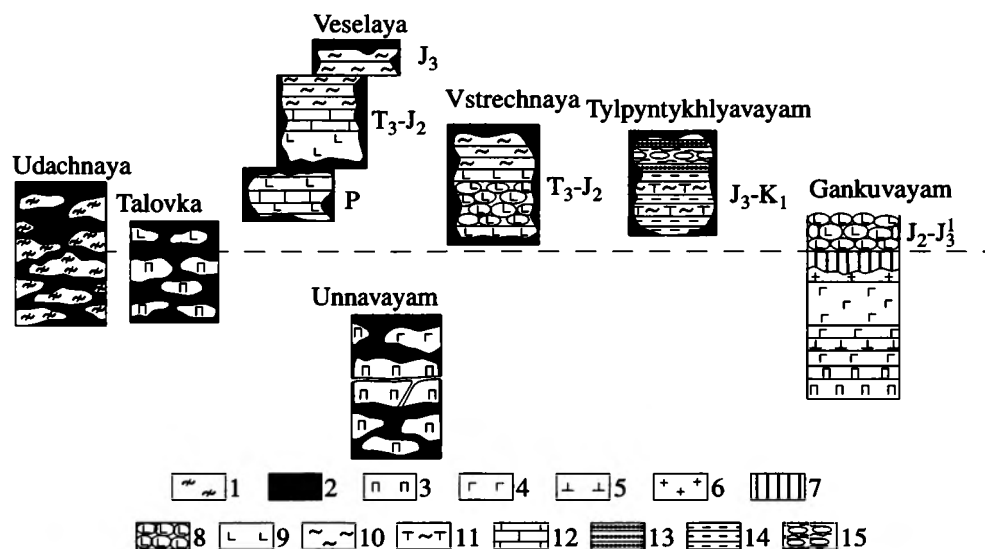


Fig. 2. Composition of the principal tectonic slabs of the Kuyul Ophiolite Terrane. (1) Amphibolites and green shales; (2) serpentinites; (3) peridotites; (4) gabbro; (5) wehrlites; (6) plagiogranites; (7) parallel dikes; (8) pillow lavas; (9) basalts; (10) cherts and jaspers; (11) tuffite jaspers; (12) limestones; (13) sandstones; (14) aleuropelites; (15) olistostrome.

decrepitation temperature of sulfides varies within 100–280°C; the sulfur isotope composition in pyrites is very close to the values obtained by H. Kawahata for pyrite from Site 504B near the Galapagos spreading center (Fig. 3). Compared to pyrites from Juan de Fuca Ridge and a hydrothermal field at 21°N on the East Pacific Rise (EPR), the Gankuvayam varieties are enriched with heavy sulfur isotopes and are similar in this aspect to the Troodos Massif sulfides.

The Gankuvayam slab does not contain effusives altered to smectite metamorphic facies, which is characteristic of the upper parts of many ophiolitic sections, including the Troodos Massif and Site 504B (Chudaev *et al.*, 1993). V.B. Kurnosov, one of the authors of the aforesaid paper, suggests that this part of the section, which has a thickness of a few hundred meters, was not preserved in the Gankuvayam slab. This is also in line with the absence in the slab of relics of the sedimentary cover overlying the basalts. It is possible that the ferromanganese ore occurrences, similar to those in the Troodos Massif sedimentary cover and sediments of the Galapagos geothermal field, used to exist in the Gankuvayam slab.

Mainitsa Terrane. This is one of the most complicated and heterogeneous structures of the Koryak Highland, and is known as the Mainitsa Zone (Ruzhentsev *et al.*, 1982). It comprises large serpentinite melanges, such as Verkhnekhatyrsk, Yagel'noe, and others, as well as slabs of different-age (Late Triassic, Late Jurassic, and late Tithonian–Neocomian) deposits, which are especially widespread. In the southwestern part of the of the Mainitsa Zone (the Emravaam–Pikas'vayam Nappe system), the late Tithonian–Neocomian deposits, which are normally attributed to the Chirinaï Group, form at least two different (in facies composition) slabs separated by the Verkhnekhatyrsk serpentinite melange (Sokolov, 1992). The Mainitsa Zone is characterized by a wide development of clastic sediments (tuffs and compositionally variable sandstones, largely graywacke, but sometimes more mature oligomictic quartzose varieties) that occur among different-age deposits, including the Chirinaï Group. Locally, the Chirinaï Group deposits, which are usually thought to be sediments of a marginal sea (Ruzhentsev *et al.*, 1982), are intensively broken down and altered to initial high-pressure metamorphic grade. According to Sokolov (1992), the Chirinaï Group corresponds to the concept of "broken formation," proposed for the characterization of the highly similar (in the tectonic metamorphism grade) Franciscan Formation of California.

The manganese ore occurrence under consideration is situated within the Emravaam–Pikas'vayam Nappe system among of the upper Chirinaï slab deposits. The ore body occurs in a Tithonian–Neocomian jaspers stratum within terrigenous deposits in the core of a recumbent fold. The contacts between siliceous and terrigenous rocks are disturbed by detachments. The ore-bearing rock forms a bed whose thickness in swellings

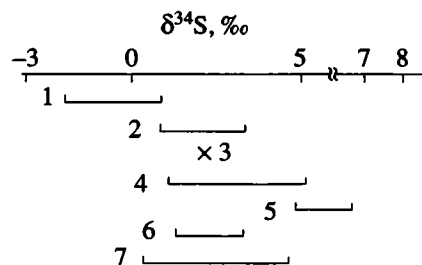


Fig. 3. Sulfur isotope ratios in pyrites from the Gankuvayam slab as compared with basalts, pyrites, and solutions from different submarine hydrothermal fields (Chudaev *et al.*, 1993). (1) Oceanic basalts; pyrites: (2) EPR 21°N, (3) Juan de Fuca Ridge, (4) DSDP Site 504B, (5) Gankuvayam slab; solutions: (6) EPR 21°N, (7) DSDP Site 504B.

reaches 2 m and apparent length in the fold is not less than some tens of meters. The ore-bearing rock is distinguished by its black color on the background of the red jasper and surrounding gray sandstones. The ore consists of a framework of segregated manganese oxides with relic colloform texture. The mineral form of the oxides has not been studied. The spaces between manganese oxide clots are filled with manganocalcite (?), almost isotropic zeolite, and chlorite. Spheroidal sinters, which are made up of an alternation of manganocalcite and zeolite laminae, are locally developed. Sometimes manganocalcite crystals may be observed growing on the manganese oxides, which deform the zeolite interlayers but do not pierce them.

Chemical composition of the rocks is listed in Table 1 (Sample G 583/5). Because the most part of Mn is in the Mn^{3+} and Mn^{4+} forms, the total content of oxides is low. The contents of Ni, V, Cu, and Co in the ore mass, given in the table, are several times less than those in oceanic ferromanganese concretions, testifying to the nonhydrogenic nature of the ores under consideration. Their hydrothermal sedimentary origin, with a faster accumulation of ore matter, is more plausible.

Study of ore sediments associated with the discharge of hydrothermal systems on the ocean floor and ore occurrences in effusive siliceous formations accreted in continental orogenic belts showed that manganese hydroxides normally settle after the precipitation of chalcophile elements (in the form of sulfides) and iron hydroxides during the migration of hydrothermal solutions. Iron hydroxides accumulate either in free form or as ferruginous–siliceous gels that afterwards can transform into ferruginous smectite. The well-known fractionation of iron and manganese in sedimentary process results from the fact that within the natural range of pH, the manganese mobility is retained even when values of Eh are several hundred millivolts higher. For example, at pH 8, the reaction potential for the transition into insoluble oxide forms is –200 mV for $Fe^{2+} \rightarrow FeOOH$ and +500 mV for $Mn^{2+} \rightarrow MnO(OH)_2$ (Rozanov *et al.*, 1976; Strakhov, 1976a). In the case at hand the precipitation of colloidal

Table 1. Chemical composition of hydrothermal sedimentary metalliferous and ore-bearing rocks in effusive siliceous formations of the Koryak Highland

Sample no.	G-738/20	G-738/21	M-405/10	M-389/5	M-389/6	M-398/7'	M-368/4a	M-368/4b	G-583/5
SiO ₂	55.00	37.68	66.5	31.80	25.24	31.66	14.74	13.18	20.92
TiO ₂	0.26	0.60	0.39	0.43	0.49	0.45	0.88	0.98	0.04
Al ₂ O ₃	5.00	7.93	4.48	3.67	4.47	3.84	5.44	5.75	1.69
Fe ₂ O ₃	20.89	36.89	18.68	42.55	44.95	39.81	60.11	62.28	0.89
FeO	0.36	0.48	0.19	0.86	0.39	0.90	5.67	5.21	0.00
MnO	7.00	5.70	3.25	8.10	8.20	10.80	0.44	0.45	51.19
MgO	0.65	0.97	2.31	3.08	3.20	3.08	4.40	4.53	0.40
CaO	6.44	6.28	1.22	5.06	6.76	4.72	3.15	2.62	3.81
Na ₂ O	0.25	0.35	0.53	0.28	0.17	0.15	0.16	0.18	0.03
K ₂ O	0.18	0.35	0.36	0.14	0.35	0.22	0.22	0.32	0.13
P ₂ O ₅	1.35	0.27	0.28	1.28	2.11	0.98	0.95	0.86	—
CO ₂	—	—	—	—	—	—	—	—	4.45
L.O.I.	2.58	2.25	1.94	2.90	3.48	3.22	3.99	3.78	7.69*
Total	99.95	99.75	100.13	100.15	99.81	99.83	100.15	100.14	91.90
Cr	163	76	—	93	—	95	140	205	18
Ni	245	325	—	365	—	340	88	96	185
V	200	330	—	260	—	250	265	270	86
Cu	130	127	—	147	—	115	15	18	44
Co	32	38	—	60	—	57	9	10	6
Pb	37	42	—	50	—	50	5	5	—
Ge	3.0	3.2	—	2.2	—	2.3	3.5	3.5	<3
Mo	2.6	1.5	—	4.7	—	4.4	3.2	3.5	3.1
M-Ti	127	85	67	141	132	137	89	81	2000
M-Al	0.12	0.12	0.13	0.05	0.06	0.05	0.06	0.05	0.03

Notes: Content of oxides is given in wt %, minor elements in ppm; (—) not analyzed; * sum of H₂O⁺ and H₂O[−]. Silicate analysis was carried out by classic wet method at the Central Analytical Laboratory PGO Ukrchermettegeologiya, Kerch (samples G-738, M-405, M-389, and M-368) and the Analytical Center of GIN, Russian Academy of Sciences (sample G-583). Content of minor elements was determined by quantitative emission spectral analysis at Analytical Center of GIN.

$$\text{M-Ti (titanium modulus)} = \frac{\text{Mn} + \text{Fe}}{\text{Ti}}; \text{M-Al (aluminum modulus)} = \frac{\text{Al}}{\text{Al} + \text{Fe} + \text{Mn}}.$$

particles of manganese oxides is most likely to have occurred at low hydrothermal activity, when other elements could precipitate by the ascent of solutions to the surface. However, it is not excluded that the ore body formed at some distance from a hydrothermal vent, but, due to scarcity of natural exposures, the traces of lateral changes in the ore body were not preserved. Judging from the textural relationships, manganese carbonate, zeolite, and chlorite probably settled at a postsedimentary stage.

Yanranai Terrane. It is best exposed within the Yanranai Dome that represents in the modern structure a tectonic window among the nappes of the Ekonai Zone (Ruzhentsev *et al.*, 1982). The structure of the Yanranai Dome was most thoroughly discussed by Grigor'ev *et al.* (1987). The dome consists of at least four slabs with an age interrelation typical of accretionary prisms: deposits of any overlying slab are older than those of the underlying slab (Fig. 4). The lowermost

position is occupied by a slab whose succession is terminated by a Maestrichtian olistostrome including fragments of the overlying slabs. The uppermost slab is of Late Tithonian–Neocomian age. The age of the two middle slabs is similar and falls within a range from the Turonian to Campanian, but the facies types of their deposits differ from each other, particularly in the Campanian part of the succession. In the overlying slab, Campanian deposits are made up of terrigenous turbidites a few hundred meters thick.

Iron-bearing metalliferous deposits were encountered between two slabs (Fig. 4). The iron ore deposits in these slabs differ by their position in the section, interrelation with effusive complexes, composition, and facies conditions of accumulation.

In the effusive siliceous member of the upper slab, on the surface of one of the flows of pillow amygdaloidal spilites alternating with hyaloclastites, lenslike accumulations of ferruginous jasper-quartzites associ-

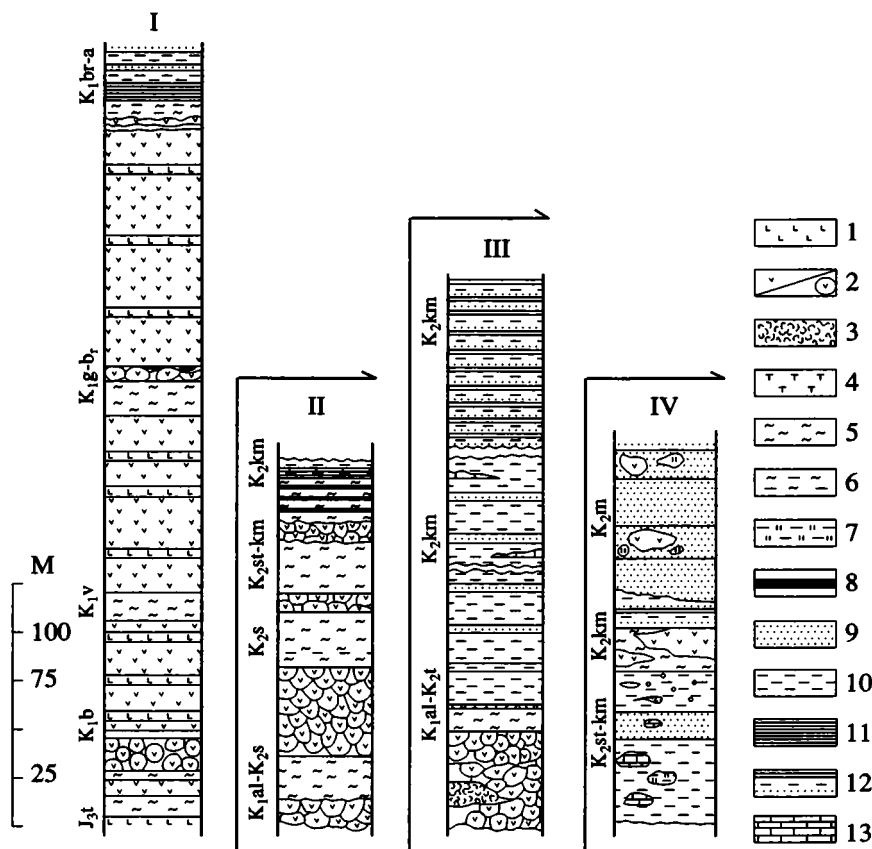


Fig. 4. Stratigraphic sections and interrelations of tectonic slabs in the Yanranai Dome. Slabs: (I) Yakanuveem, (II) Yakenmyveem, (III) Vaamychgyn, (IV) olistostrome. (1) Diabases, (2) basalts and pillow lavas, (3) hyaloclastites, (4) basic tuffs, (5) jaspers, (6) cherts, (7) clayey cherts, (8) hydrothermal sedimentary metalliferous deposits, (9) sandstones, (10) aleuropelites, (11) mudstones, (12) turbidites, (13) limestones.

ated with thin ore crusts are observed. The jasper-quartzites fill depressions in the relief of the lava flow surface. They are composed of granular quartz with hematite fringe. There is no evidence for the former presence of biogenic siliceous material. The Fe_2O_3 content in the jasper-quartzites reaches 10 wt %. Gel dehydration fissures are observed on the swelling surface of the jasper-quartzites. The fissures are filled with ore-free quartz. The ferruginous crusts associated with the jasper-quartzites are up to 5 cm thick. In places, they rest directly on top of basalts. The crusts are composed of massive hematite that constitutes the main part of iron oxides in the bulk chemical composition of the rocks (Table 1; samples M-368/4a and M-368/4b). Hematite matrix is cross-cut by abundant epidote segregations of two generations. The earlier one forms micronodules and lenslets which tend to be concentrated on loop-shaped surfaces. The bent surfaces seem to be related to microslump structure of the ore-bearing rocks. The later generation, filling fissures, is formed by coarser-crystalline epidote, along with quartz and Mg-chlorite. The chemical composition of these crusts is characterized by a very low content of Mn, Ni, Cu, and Co and a relatively high content of Ti, Cr, and V

(iron group elements). There is observed a very low concentration of REE, with the prominent negative Ce anomaly (Table 2) characteristic of some types of deep-water oceanic deposits rich in iron hydroxides of hydrothermal sedimentary origin.

Iron-rich, hydrothermal sedimentary metalliferous deposits at the base of oceanic sedimentary cover were recovered by some deep-water boreholes in the Pacific, Indian, and rarely in the Atlantic oceans, and they were described in many papers. Particularly thick basal iron ore sediments were drilled at Sites 294 and 295 in the West Philippine Basin (Bonatti *et al.*, 1979). Their thickness between the sites varies within a few tens of meters. However, most of these basal metalliferous sediments contain detectable amounts (some wt %) of Mn and differ from the abovementioned crusts by a higher content of Ni, Co, and Cu (manganese group elements). They do not differ in their chemical composition from metalliferous sediments from the upper levels of the oceanic sedimentary cover of the southeastern Pacific Ocean (Dekov, 1994; Dubinin and Volkov, 1987, 1992; *Metallonosnye ...*, 1979).

A low Mn content in iron oxide accumulations was noted within a geothermal field of the EPR spreading

Table 2. REE abundances (ppm) in hydrothermal sedimentary metalliferous and ore-bearing rocks from effusive siliceous formations of the Koryak Highland

Sample no.	G-738/20	M-405/10	M-389/7	M-368/4b
La	134.0	32.1	95.4	15.1
Ce	24.1	8.2	16.4	3.0
Nd	114.0	32.5	86.5	19.6
Sm	29.1	7.5	22.4	5.36
Eu	4.4	1.69	6.0	1.41
Gd	29.8	8.44	20.06	7.34
Dy	27.8	—	—	—
Er	15.1	3.18	10.8	5.6
Yb	11.0	2.96	8.84	5.55
Ce _n /Ce _n *	0.08	0.11	0.08	0.08
ΣREE/Fe*	26.1	7.3	9.3	1.1

Notes: * Analyses were carried out by atomic emission method with inductively coupled plasma (I.F. Seregina, Analytical Center of GIN, analyst) $Ce_n^* = (La_n + Nd_n)/2$; contents are normalized to PAAS. (Fe*) total iron content. (—) Not analyzed.

zone at 21°N. However, Francheteau *et al.* (1979) showed that these accumulations are secondary ochres originating as a result of oxidation of pyrite ore. For the crusts being considered, such scheme of their formation is supported neither by their mineral composition nor by the structural and textural peculiarities.

They are of the approximate geochemical composition of ferruginous-silicate hydrothermal sedimentary ore-bearing deposits (Butuzova, 1989). The association of these ferruginous crusts with ferruginous jasper-quartzites is not likely incidental. We think that the formation of such hydrothermal sedimentary deposits was conditioned mainly by a temperature fall at that time and the corresponding sharp decrease of silica solubility rather than by changes of pH and Eh of hydrothermal solutions as they mixed with near-bottom water. It is common knowledge that this would lead to the settling of silicic or (more frequently) ferruginous-silicic gel. It should be noted that by their Mn content these crusts are similar to the basal metalliferous deposits that overlie basic lava flows in the Oman successions (Fig. 5) (Fleet and Robertson, 1980; Robertson and Fleet, 1986). To explain the relatively high content of TiO₂ in the crusts, the interesting conclusions drawn by Dubinin and Volkov (1987, 1992) can be applied. According to them, within the axial zone of the EPR, up to 75% TiO₂ may not have lithogenic origin and may not be incorporated into silicate matrix. The accumulation of Ti should presumably be explained by its sorption on fresh colloids of iron hydroxides.

The other, intraformational type of metalliferous sediments of ferromanganese composition was encountered in the Upper Cretaceous effusive siliceous sequence constituting Yakenmyveem slab (Fig. 4). One of the members of this slab contains dark-brown metal-

liferous siliceous rocks. These rocks form interlayers 2 to 10 cm thick (averaging 3 to 4 cm), which alternate with thicker layers of red radiolarian jaspers. The total thickness of this alternating member is about 5 m. It is characterized by Santonian-Campanian radiolarians, has a good continuity in the section, and is traced over a distance of about 5 km. Hence, the area of the metalliferous sediments in the slab is not less than a few tens of square kilometers.

The rocks are made up of opaque (in thin sections), dark red-brown matter. The material of the host jaspers is observed only in places. Reflections of quartz and hematite are clearly expressed in all X-ray diffraction patterns. The presence of birnessite is indicated by a small peak at 7.20 Å that disappears after the treatment with a hydroxylamine-containing agent according to the procedure developed by Shterenberg (1973). Other mineral phases are not observed in the diffraction patterns.

The chemical composition of these rocks is listed in Table 1 (samples M-389/5-7, M-405/10, and G-738/20, 21). On the basis of Mn, Fe, and Si ratio they completely fall within a field of metalliferous sediments of the EPR slopes and the Bauer Deep (Fig. 5). The increased content of P₂O₅ in ore interlayers is worthy of notice. No special studies to elucidate the phosphate mineral phase were carried out. The content of heavy metals in the studied samples varies within a few hundred parts per mille, which is compatible with their content in metalliferous oceanic sediments and the Cyprus and Oman umbers (Dubinin and Volkov, 1987, 1992; Fleet and Robertson, 1980; Kaleda and Krylov, 1992; Robertson and Fleet, 1986; Robertson and Hudson, 1973; *Metallonosnye* ..., 1979). A total REE content and their specific content relative to iron hydroxides is several times higher in the studied metalliferous rocks than in the crusts described above (Table 2). Based on the investigations by Dubinin and Volkov (1987, 1992), this difference can be explained by a larger distance of the deposition centers of the intraformational metalliferous siliceous rocks from zones of hydrothermal activity. Their REE patterns are similar to those observed in the crusts and they are characterized by the close values of a Ce negative anomaly. This hydrogenic anomaly, a peculiar "oceanic marker," indicates deep-water, pelagic conditions of accumulations of these sediments.

Many researchers, including a large group of Russian oceanologists (Yu.A. Bogdanov, A.P. Lisitsyn, and many others), associate the accumulation of intraformational hydrothermal sedimentary metalliferous sediments in young deposits on slopes of the EPR with the increase of hydrothermal activity during the periods of the higher spreading rate (*Metallonosnye* ..., 1979). A similar explanation can be applied to the origin of the Santonian-Campanian metalliferous deposits from the Yakemyveem slab of the Yanranai Dome, especially since similar metalliferous rocks appear at the same strati-

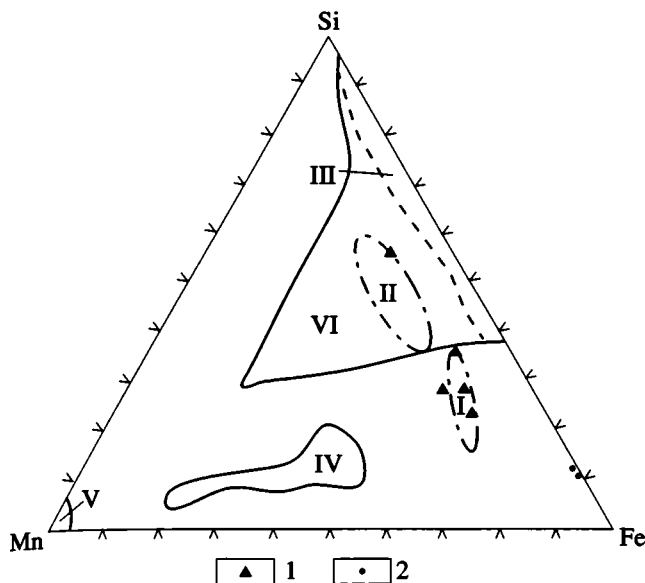


Fig. 5. Fields of different metalliferous hydrothermal sedimentary accumulations in Fe-Mn-Si diagram (Robertson and Fleet, 1986) and position of the Yanranai metalliferous deposits. (1) Intraformational Santonian-Campanian metalliferous deposits of the lower slab, (2) basal ferruginous crusts associated with jasper-quartzites from Neocomian sequence of the upper slab. Fields in diagram: (I-II) metalliferous sediments: (I) EPR, (II) Bower Basin, (III) veined interstices, mounds, and sediments overlying basic lavas in Oman, (IV) deep-water concretions from the Bauer Deep, (V) hydrothermal sediments of the Mid Atlantic Ridge and Galapagos Rift; (VI) Oman umbers.

graphic level in some slabs of the Vatyn Formation in the Olyutor Zone in the southern Koryak Highland. The area occupied by metalliferous sediments in the western Pacific in the Late Cretaceous was probably by several orders of magnitude larger than the area of their distribution in the Yanranai Dome. The zone of hydrothermal activity which produced this mineralization is believed to have been situated within an assumed Late Cretaceous spreading center, separating the Kula Plate from the Vaamuchgyn Plate. Fragments of the latter were incorporated into accretionary structures of the Koryak-Kamchatka rim of the Asian continent (Grigor'ev *et al.*, 1994).

CONCLUSION

From the foregoing, it is seen that among effusive siliceous deposits of the Koryak Highland, there are hydrothermal and hydrothermal sedimentary ore occurrences that could be correlated with the corresponding ore occurrences in some tectonomagmatic structures of the Pacific Ocean. They are discrete areas within the central part of the EPR and its northwestern slope, including the Bauer Deep and Juan de Fuca Ridge, and the Galapagos rift zone system (*Geologicheskoe ...*, 1990; *Metallonosnye ...*, 1979). Hence, the peculiarities of metallogeny of effusive siliceous rocks well con-

form with the previous conclusions drawn on the basis of other evidence for their oceanic origin.

The ore manifestations similar to those in the above listed oceanic structures were found recently in back-arc basins of the central Pacific Ocean, from the Philippine Sea on the west to the Lau Basin on the east. These intraoceanic seas are situated between the Indoaustralian, Eurasian, and Pacific plates whose relative movement defined at least the Cenozoic evolution of this belt (Zonenshain and Khain, 1990). It is likely that in these confined sedimentary basins, an oceanic-type hydrothermal activity can affect sedimentation more strongly than in more open oceanic structures, and, consequently, the relative importance of hydrothermal sedimentary deposits in the sedimentary cover may increase. The peculiarities of metallogeny of the above indicated basins were considered in part by Lisitsyn *et al.* (Lisitsyn, 1991; Lisitsyn *et al.*, 1992a; Lisitsyn *et al.*, 1992b). We think that this can partially explain the clearly displayed hydrothermal sedimentary ore accumulation in suprasubduction Mesozoic deposits of ophiolitic sections of Oman, Syria, and Cyprus.

From the information currently available, it follows that mineralization in the similar in age oceanic complexes accreted in the Koryak-Kamchatka orogenic belt and on the west of Central and South America differs in scales. Within the American onshore zone, ore occurrences, including relatively large ones, are more often encountered. This pattern is likely to reflect the different degree of preservation of oceanic complexes in accretionary structures in the western and eastern continental rims of the Pacific Ocean and different details of their investigation.

The Santonian-Campanian intraformational metalliferous hydrothermal sedimentary deposits in the Koryak Highland deserve special attention. It is probable that their appearance is related to tectonic activation of the oceanic floor at that stage of the Pacific evolution.

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Peculiarities of Lithogenesis of the Pre-Cenozoic Deltaic–Marine Complexes in the Basins of Different Types (Northern Siberia): Communication 2. The Basin with Undercompensation Sedimentation in the Verkhoyansk Region

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Abstract—The signs of similarity and distinction of the processes of sedimentogenesis and lithogenesis in the deltaic–marine Paleozoic and Early Mesozoic sediments of the Verkhoyansk Miogeosyncline, and also the Late Mesozoic sediments of the Verkhoyansk Foredeep, are compared with the Early Mesozoic formations of the Koltogor–Urengoi Graben Rift located in the base of the epi-Paleozoic West-Siberian Platform described in the previous communication. Explanations are given for the distinctions in the lithogenetic processes, depending on a particular formational and paleotectonic affiliation of the deltaic complexes.

INTRODUCTION

In the previous communication, we analyzed the peculiarities of sedimentogenesis and lithogenesis, with reference to the Early Mesozoic deltaic–marine sediments of the Koltogor–Urengoi graben rift. These sediments accumulated in the conditions almost corresponding to the compensation filling of a rapidly subsiding depression, at $B/L \geq 1$ (where B is catchment area, L is drainage basin area). It was noted that miogeosyncline troughs belong to an essentially distinguished category of tectonic structures, where the main sedimentary pile, despite an avalanche speed of its accumulation, had no time to compensate the impulsive and rather deep subsidences of the substrate. The variable paleotectonic conditions were reflected both on the vertical and lateral facies distribution in paleobasins. Additionally, values B and L in the sedimentary basins of miogeosyncline zones are many orders of magnitude more than those calculated for the taphrogenic zones, whereas the B/L ratios are lesser. It invariably influenced the specificity of the “sediment fund” composition. Hence, here we can expect a somewhat different trend of evolution of the lithogenesis, inasmuch as the process in many respects depends on a composition of initial sediments.

To illustrate these distinctions on a particular geological example, we offer the comprehensively studied Late Paleozoic and Mesozoic sedimentary complexes of the Verkhoyansk miogeosyncline folded zone.

SEDIMENTARY ENVIRONMENTS

The age of a more than 15 km thick terrigenous sequence, known in the literature as a Verkhoyansk folded complex of Mesozooids of Northeastern Siberia,

is Early Carboniferous (Visian) to Late Jurassic. The sequence is developed to the east of Lena and Aldan rivers, within the Verkhoyansk and Kular ridges, Sredne-Yanskoe Upland and adjacent territories, and represents partially preserved fragments of marine deposits of a continental margin (Natapov, 1990; Parfenov, 1984; Safronov, 1992). These deposits were subdivided into two following paragenetic facial complexes, each confined to a particular paleotectonic structure and reflecting a certain stage of a geotectonic evolution (Yapaskurt, 1992); that is, each facial complex corresponds to a genetically determined rock body or formation according to a definition given by Timofeev (1994): (1) Late Paleozoic deposits of alluvial fan system of marine basin in the paleo-Verkhoyansk Miogeosyncline and (2) Early Mesozoic, moderate deep-water deposits of marginal sea basin in the Yana-Indigirka Trough.

Within mentioned formations, many fragments of the continuous facial successions are described; one of these fragments is schematically shown in the profile (Fig. 1) constructed conditionally, without the amendments for essential tectonic (dislocational and overthrust) approachment of facies, arising as a result of a Late Mesozoic folding. The profile exhibits a structural regularity common for both formations: everywhere, across the strike of the formations, from the southwest to northeast, three characteristic facial parageneses replace each other (Fig. 1, I–III). Each of the parageneses corresponds to the major, separated element of a landscape, and hereinafter is called macrofacies. Just the macrofacies will be characterized below, inasmuch as the smaller facies together with their genetic features were described in recent works (Yapaskurt, 1992; Yapaskurt *et al.*, 1993, 1994).

I. Macrofacies of the deltaic and interdeltic shelf deposits stretches along the western border of the Verkhoyansk complex rocks. In the modern tectonic structure the maximum width of its outcrop (opposite to the Vilyui River mouth) is more than 300 km.

Most of the rock structures and textures are similar to those in the modern sediments originated as a result of traction of terrigenous substance along the bottom, saltation, "particle-by-particle" precipitation of suspension, or particle distribution by wave processes. Thus, for example, the availability of apparently monolithic sandstone units (2 to 50 and more meters thick), which consist of numerous layers with diverse kinds of cross-bedding, and superficial ripple marks of currents and wave agitation serves as an indicator of the high mobility of the sedimentary environment. High-grade sorting of clastic material, low content of clayey admixture, and other features, make these rocks similar to the sands observable in the front zones of modern and Cenozoic deltas: these sands belong to the type formed under active influence of wave processes (Elliott, 1986).

W.E. Galloway noted that the wide distribution of such sands requires tectonic displacements of substrate along the river-sea interface. According to his opinion, the most important case is when the subsidence rate of a basin bottom exceeds the rate of a sedimentary material demolition by rivers. It results in the subsidence of a prodelta base and subsequent intensification of clastic material processing by waves (*Deltas ...*, 1975).

At active tectonic movements, the thick sand accumulations arising near a delta front can be distributed far into a basin through a wedge of prodeltaic sediments and underwater systems of channels onto the bottom of a marine depression. Another mechanism of sedimentation functions there: the avalanche-like movement of a high-density flow instead of a particle-by-particle transportation (Khvorova, 1989; Stow, 1986). Obviously, many deposits related to macrofacies II and III (deep-sea environment) are formed in a similar way; such deposits are recognized in the central and east sectors of the Verkhoyansk complex area (Solov'eva and Yapaskurt, 1994).

II. Macrofacies of the prodeltaic sediments passing into continental slope fans are characterized by the following structural peculiarities: (1) wide development of the underwater slump dislocation (amplitudes ranging from 10–20 cm to 100–200 m) within the aleuopelitic sequences; (2) presence of the mixtite units containing small (a few centimeters) to large (10 m and more), sandy and coarse-aleuritic olistoliths chaotically distributed in a fine aleuritic-to-clayey matrix; (3) presence of rare unstratified sandstone beds with structural and textural features of the high-density grain flows ("grainites," according to Voznesenskaya, 1984).

III. Macrofacies of alluvial fans together with various other hemipelagic deposits are characterized by: (1) development of grainites and turbidites; (2) pres-

ence of thick (tens to a few hundreds of meters) units composed of the obscure- or irregular-stratified silty mudstones and fine-grained siltstones with high organic carbon contents ranging from 2 to 5.2% (Yapaskurt *et al.*, 1993).

Externally, the bulk of fine-grained siltstones are very similar to the Late Cenozoic and modern deposits developed in the Tatar Strait (basin of Sea of Japan) at depths about 2 km and are related to a "nepheloidite" group described and illustrated in (Likht, 1991). Externally, they are similar to distal turbidites, differing from the latter by the inconspicuous textural features, which are analyzed in the above-mentioned work. Their genesis is related to the extreme seasonal mud exportation during high waters on the rivers.

The remaining aleuopelitic rocks of this macrofacies are identical to those described by Stow as the fine-grained turbidites with wavy siltstone interlayers from the Cambrian-Ordovician Halifax Formation, New Scotland (Stow, 1986).

Most of the sandy rocks have a similar structure typical of grainites (Reineck, Singh, 1977; Voznesenskaya, 1984). These rocks are mostly unstratified, massive, and fine-grained or medium- to fine-grained; they contain well-sorted but poorly rounded clastic material, and lack intergranular clayey filling. The thickness of their layers ranges from 10 to 40 cm, less often to 1–1.5 m; sometimes, they are combined into units with thickness reaching 5–10 m or more. Their lower and upper contacts with the host mudstones are always sharp. The bottom of layers, as a rule, is uneven, locally containing the saucer-shaped molds formed by the injection of sandy material into a primarily watered silty substrate. Occasionally, vague cross-lamination features (signs of redistribution of substance by the bottom currents after a stop of a grain flow) are observed near the top of a stratum.

Some levels of a geological section, generally corresponding to the regressive eustatic stages of a sea, are marked by the presence of the sandy-aleuopelitic turbidites. In particular, they were observed by Andreev (1983) within the Permian sediments on the northeastern wall of the Boguchan deep fault (Fig. 1, columns 6, 7).

Some analogies were revealed when comparing the lithofacial compositions of the deposits of the paleo-Verkhoyansk Basin and other basins. In particular, it was revealed that, according to the sedimentation mechanisms and environments, the Upper Paleozoic deposits of North Verkhoyansk region are very similar to the Lower Carboniferous deposits of northern England, comprehensively characterized in the literature thirty years ago (Allen, 1960; Collinson, 1968, 1969; Walker, 1966). According to the structural and textural features and peculiarities of the vertical and lateral combinations, all the facies recognized in the northern England and Verkhoyansk region have appeared identical.

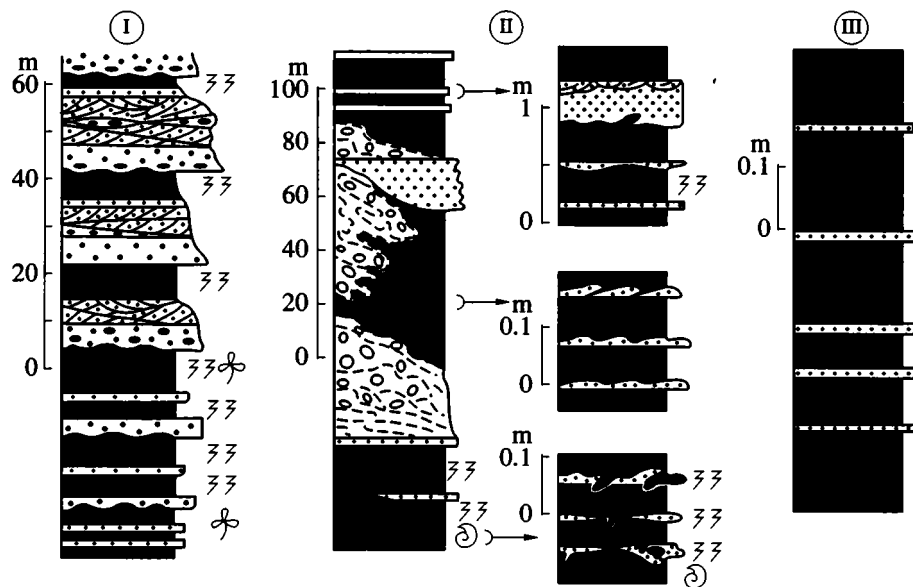


Fig. 1. Fragments of typical geological section (above) and schematic lithofacial profile (below) of a sector of the Verkhoyansk complex (Carboniferous–Lower Permian) (modified after Yapaskurt, *et al.*, 1993; Andreev, 1983. Legend on the profile facies: (1) delta and avandelta channel front, (2) avandelta lobes and interlobate areas of shelf, (3) prodelta and continental shelf, (4) the same, with slump dislocations, (5) hemipelagic cones and sink-holes; geological boundaries: (6) stratigraphic (the inferred boundaries are shown by a dotted line), (7) facial, (8) tectonic; (9) terrigenous carbonate deposits of the Devonian and Tournaisian (D_3 – C_1); (10) mainly carbonate deposits of the Cambrian and Precambrian (P_1 – C_3); (11) location and numbers (I–III) of the fragments of typical microfacies sections (names see in the text). Legend on the inset. (12) Western Verkhoyansk marginal suture; (13) other deep faults: (B) Boguchan, (D) Dzhardzhan, (U) Unguokhtakh; (14) key sections and their numbers (encircled): (I) Uyel-Siktyakh River, (2–3) middle and lower reaches of Soguru-Uyel-Siktyakh River, (4) Meichan River, (5) upper reaches of Kharaulakh River, (6) Oiun-Yurege River, (7) Kuolai River). Legend in the columns: (15) intraclasts in gravelstones and sandstones; (16) coarse- and medium-grained, massive sandstones; (17) the same, with cross-bedding; (18) fine-grained sandstones and siltstones; (19) silty mudstones; (20) mixtites with subwater slump dislocations; (21) bioturbation textures; (22) inclusions of the terrestrial flora remnants; (23) inclusions of marine fauna.

On the profile, the top of Lower Permian deposits are adjusted to a zero level, numbers above the zero level denote key sections (see on the inset). Indexes designate of the Carboniferous and Lower Permian formations: (C_1 bl– C_2 st) Bylykat and Setachan formations (undivided), (C_2 jp) Yupenchin Formation, (C_2 -3sd) Sieder Formation, (P_1 un) Unguokhtakh Formation, (P_1 hl) Khaldzhin Formation.

Hence, the reconstructed models of the marine paleobasins and sedimentary environments essentially correspond to each other (Walker, 1966; Yapaskurt *et al.*, 1993).

Both basins are characterized by similar shape and high accumulation rate of sediments delivered into the sea through deltas and redistributed by high-density flows. The latter formed fan lobes in a bathyal zone of the sea. Judging from the circumstantial signs (thickness of the subwater slump dislocations and analogy to the recent deposits), the maximum depth of the Verkhoyansk region basin could reach 1.5–2.5 km.

Despite the avalanche-like sedimentation rate, this depression remained uncompensated for a long time. That is why the considered complex greatly differs from that developed in the Koltogor–Urengoi Graben Rift (Yapaskurt *et al.*, 1979).

Paleozoic deposits of the Verkhoyansk region are represented by a much more diverse spectrum of facies and more multicomponent composition of the sediment fund, which underwent a complex evolution in a geological time (Fig. 2). Only the earliest stage (transition

from a last phase of the Middle Devonian rifting to the scattered spreading in Viséan) was similar to the evolution of sediment fund at a taphrogenic tectonic regime.

Subsequently, the intensive expansion of the areas of provenances and the periodic uplifts and peneplanation of a drainage surface resulted in the periodic changes in the composition and maturity of a clastic material in deltaic sediments. Therefore, the geological section of the Verkhoyansk complex demonstrates cyclic alternation of the graywacke–quartz, graywacke–feldspar, and arkose–graywacke terrigenous mineral associations with the mesomictic and siliciclast–quartz ones.

In addition to the general regional regularities in a sediment fund variability, we can observe the more individual (intraformational) distinctions dependent on a facial sedimentary environment. For example, the deltaic facies sandstones always differ from the grainites by a more polymictic composition.

The above mentioned peculiarities of sedimentogenesis are certainly reflected on the specificity of lithogenetic processes.

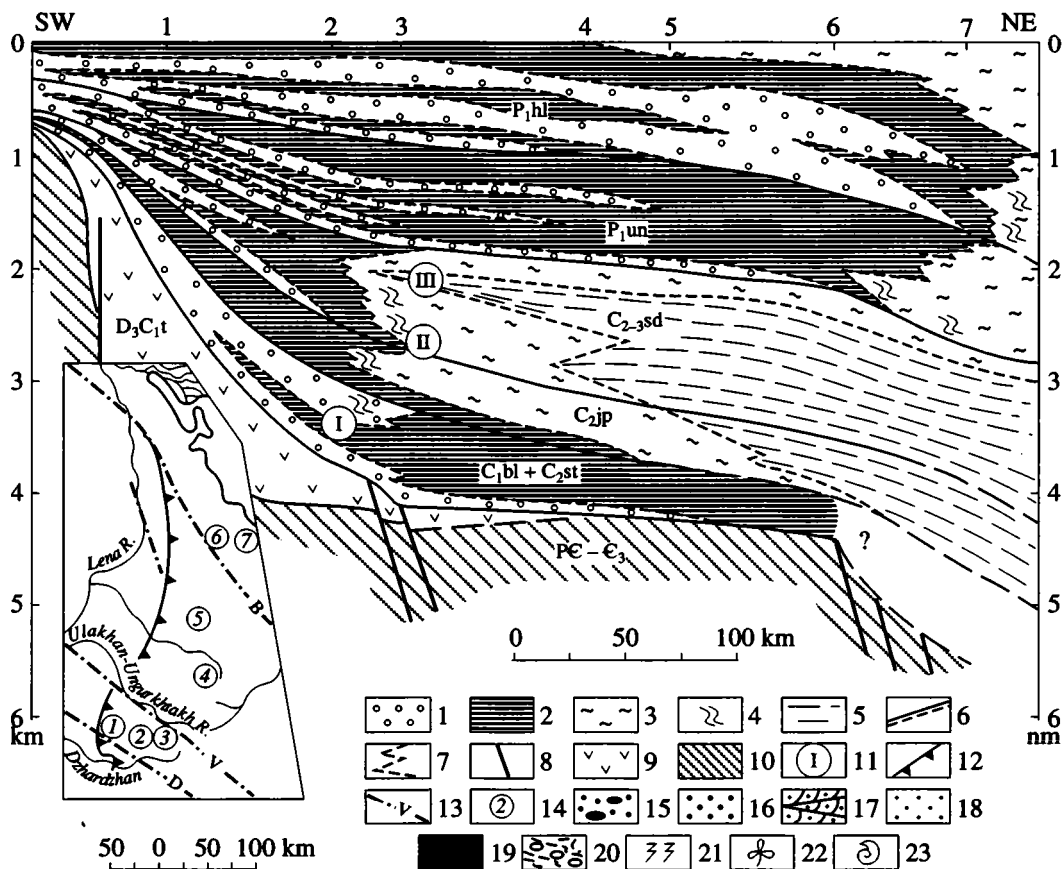


Fig. 1. (Contd.)

PECULIARITIES OF LITHOGENESIS

The postsedimentary transformations of the Verkhoyansk complex occurred in the three prolonged stages: (1) intensive subsidence of the deposits in the Late Paleozoic and Early Mesozoic; (2) inversion of the tectonic structure of sedimentary basin and formation of folded structures in the late Mesozoic; and (3) orogenic movements in the Cenozoic.

Among the numerous factors influencing the formation and changes of rocks, two are especially appreciable: inheritance of a facial sedimentary environment and composition of a sediment fund. Below we give a more detailed illumination of this aspect.

The first stage (subsidence of sedimentary basin) includes three substages: diagenesis, catagenesis, and early metagenesis.

The interrelations between lithogenesis and facial affiliation of sediments can be revealed by comparison of variations of the compositions and structures of the coeval rocks that are granulometrically similar to each other but related to the different facies. This is most vividly exemplified by the comparison of various sandstones. As was found out, the most important factor influencing the intensity of their postsedimentary transformations was the sedimentogenic clayey intergrain fill-

ing or matrix (Pettijohn, 1977). With other conditions being equal, its amount appeared inversely proportional to the degree of a sandstone alteration (Fig. 3).

The reason is the following: when the matrix is absent or is present in minor quantities, the free pores are filled by water (thalassogenic or elisional), that provides favorable conditions for an authigenic mineral genesis. On the contrary, where the grains are enveloped with a pasty clayey substance, the structural and compositional changes in rocks occurred slower and not as appreciably.

According to the mode of saturation with matrix all sandy lithotypes (sandstones) of the Verkhoyansk complex can be divided into four types: (1) without matrix (I-P), (2) matrix constitutes no more than 1-15 vol % (II-P), (3) predominant matrix as pore silty-clayey cement (III-P), and (4) predominant matrix as basal silty-clayey cement (IV-PAC). It can be seen that according to the western classifications, sandstones of varieties I-P and II-P correspond to the arenite class, the rest, to the wacke class (Pettijohn *et al.*, 1972). As it will be shown below, the given typification proved to be very convenient for the analysis of secondary changes in sediments at similar stages of lithogenesis.

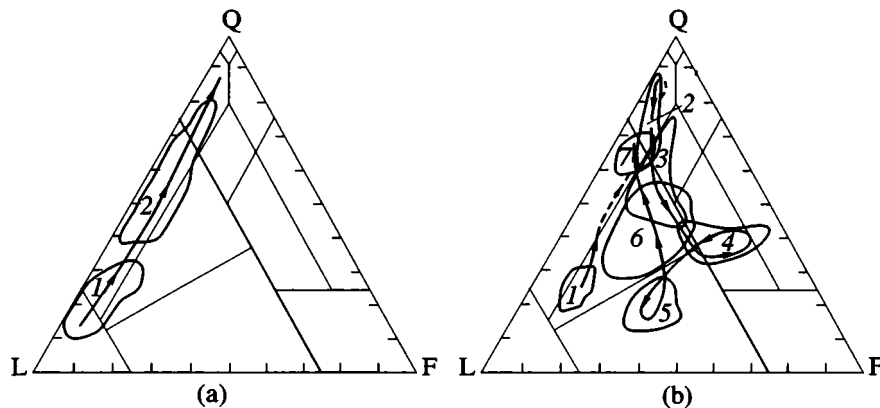


Fig. 2. Composition of clastogene sandy substance in (a) deltaic deposits of Koltogor-Urengoi Depression and (b) northern sector of Verkhoyansk Miogeosyncline. Fields of data points of deposits: Fig. 2a. (1) T_1 ; (2) T_{2-3} and J_1 ; Fig. 2b. (1) D_{2-3} ; (2) C_1 ; (3) C_{2-3} (bottom); (4) C_{2-3} (top); (5) P_1 ; (6) P_2 and T_1 ; (7) T_3 . Letter designations: (Q) quartz, (F) feldspars, (L) lithoclasts and mafic minerals.

Facies of the sandy deposits in the delta front and submarine troughs of an avandelta consist mostly of II-P and less commonly I-P type arenites. They were subjected to prolonged reworking by waves, and at some localities by wind, and therefore are much depleted in the matrix. Fragments of matrix are represented mainly by the films around the separate sand particles, or as partial fillings of voids. Their presence has a positive effect on the preservation of sedimentogenic features during deep postsedimentational alterations, e.g., at the stage of metamogenesis, in particular, when the processes of regeneration, gravitational corrosion, and recrystallization-granulation blastesis become active along the contacts between clastic particles.

On a background of the abovementioned neoformations, the clayey-micaceous edgings of a primary matrix are still observed. Microscopically, they are distinctly appreciable without the analyzer, and according to their shape, it is possible to reconstruct a sedimentogenic structure in conditions of an intensive crystallization-granulation blastesis (even at the greenschist and amphibolite stages of metamorphism).

Peculiarities of lithogenesis of the adjacent facies developed within the interchannel parts of an avandelta are somewhat different because the deposits have essentially distinctive structural and textural features. These deposits differ by a weaker sorting of the terrigenous material, owing to its intensive bioturbation and mixing by waves. Wacke varieties III-P and IV-PAC are widespread here. Most of their sandy particles are dispersed in the matrix; therefore, even at the stages of metamogenesis and early metamorphism they are deprived of both the conformal and blastic structures. Therefore, the rock looks only slightly changed in the thin sections (Fig. 3e). However, the precise investigations testify that under influence of the thermodynamic factors the intergrain matrix composition is much changed and clayey components are partly subjected to polytype modification.

For example, at the substage of late (deep) catagenesis, the smectite group minerals were transformed to a mixed-layer phase and hydromica, and partially—to chlorite. At metamogenesis, the 1 Md polytype hydromica transformed to 2M₁ variety.

All these and other transformations of clayey matrix occurred by the solid-phase mineral transformations (pursuant to the mechanism deciphered by Millot, 1970).

The dispersed organic matter, which is abundant in the avandeltaic and prodeltaic deposits, served as a major catalyst of the above mentioned processes. The mechanism of influence of organic matter on the transformation of clay minerals (Zkhus and Bakhtin, 1979) suggests that the organic matter in the considered facies could generate gaseous water fluids that are squeezed into the adjacent arenite reservoirs due to lithostatic loads.

The katagenetic transformations of an elisional type occur precisely in the same manner, according to the model proposed by Kholodov (1983). One of the evidences of the efficiency of elisional process in the considered rock complex is a nonuniform cementation of the clastogene particles within the arenite units, depending on the proximity to the contacts with wacke units or aleuropelitic rocks. Cementation is most monolithic near these contacts; with transition inside the arenite layer, the cementation is discontinuous; this provides some anisotropy of physical and mechanical properties of the similar rocks in a single geological section.

In the considered cases, the formation of many authigenic minerals in cement is related to the introduction of solutions into the intergrain voids from the adjacent, essentially clayey rocks. However, in contrast to a typical model of elisional catagenesis, which assumes a passive role of sediment fund of the arenite reservoirs (Kholodov, 1983), the sand fraction minerals rendered

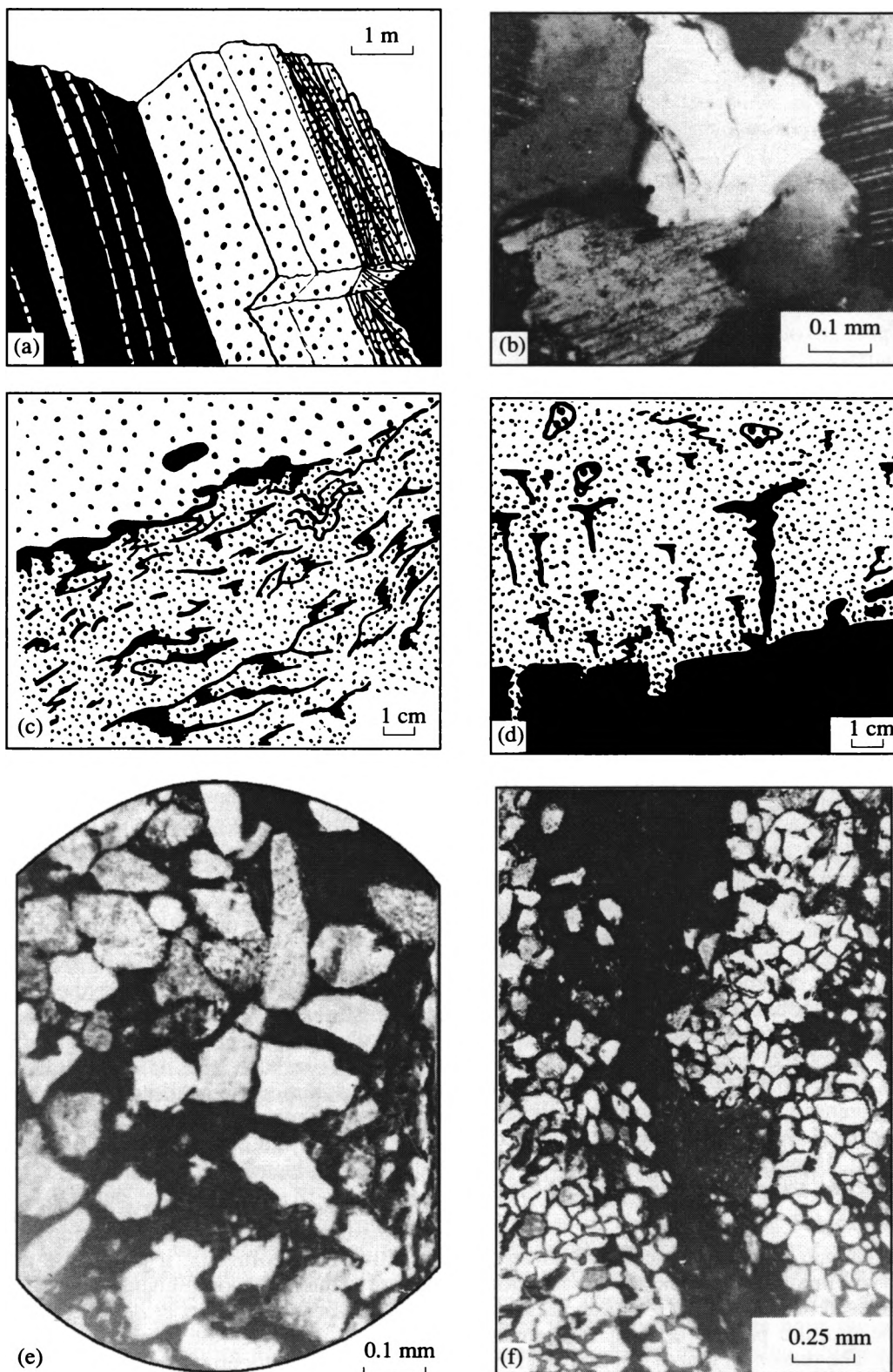


Fig. 3. Some lithotypes of the Upper Permian sandy rocks of North Khaurakh; sketches of outcrops and photomicrographs of thin sections: (a) Arenite unit I-P (black band are host aleuropelitic rocks); (b) incorporation-regeneration textures in arenite I-P (thin section, crossed nicols); (c) contact between arenites I-P (above) and wackes IV-PAC; (d) sandstone III-P occurring on clayey siltstone with bioturbation structures; (e, f) weakly deformed sedimentogenic textures in wackes IV-PAC (thin section, crossed nicols; black background is intergrain clayey matrix, saturated with fine-dispersed organic matter).

appreciable influence on the composition of authigenic components.

The direct correlation between authigenesis and sediment fund composition, which is typical of the deltaic facies of a Verkhoyansk complex, was in details described by Yapaskurt (1992), and therefore here we shall be limited only to its brief statement. For example, during the late catagenetic substage, the quartz-hydromica-chlorite cement is developed in quartz-graywacke arenites, the albite-quartz-hydromicaceous cement is found in the arcose-graywacke arenites and the regeneration quartzose cement and appreciable silicification of clastic feldspars are observed in the mesomictic and siliciclastic-quartzose arenites.

The essentially different (not previously noticed) peculiarities of catagenesis are inherent in the hemipelagic facies sediments, in which aleuropelitic rocks quantitatively prevail over the sandy ones. That is why the elisional processes were more widespread there; therefore, the greater introduction of substance from the clayey silts suppressed the influence of the sediment fund of arenites on the final results of authigenesis.

This notion is confirmed by the postsedimentation changes of grainites with the dominant I-P type arenites. Due to the best reservoir properties, the intergrain cavities of these sediments were filled by gaseous water fluids at the initial stages of lithogenesis and served as the most favorable substrate for the authigenic mineral genesis. This process could develop in two ways. According to the first mechanism, at the beginning of catagenesis, the corrosion of clastic grains and partial argillization (chloritization of biotite and hydromicization of plagioclases) of some of them was followed by an extensive calcite crystallization in the form of an interstitial or interstitial-poikilitic cement. The authigenic calcite aggregates, crystallized in free interstitial cavities without direct dependence from a grain composition, have the granoblastic textures with diverse-oriented optic axes of crystals (the mosaic extinction of carbonate grains is noticed under crossed nicols). The grainite varieties, cemented by 20–40 vol % calcite at the beginning of catagenesis, continue to retain their patterns without essential changes up to the beginning of the metamorphism. However, the minor calcite could be again dissolved on the subsequent stages of lithogenesis (Yapaskurt *et al.*, 1997).

Another mechanism of postsedimentation mineral genesis is observed in sites where the carbonatization was poorly expressed or absent due to certain reasons. In this case, the grainite pattern is most intensively changed (Fig. 4). The reason is, first of all, that at sharp increase of lithostatic pressure on a clastic framework, the congestion of terrigenous particles of an initial sediment favors the crystallization of a regeneration quartz, and also to the wide development of the conformal and incorporation textures of the gravitational corrosion.

From the late catagenetic substage, such rocks represent metasandstones, because more than 90% of their clastic components have lost the features of their sedimentogenic shape and size (Fig. 3b). Besides, their primary shapes are deformed by the following (specific for the metagenetic stage) neoformations: recrystallization-granulation blastesis of quartz (Fig. 5), silicification and partial albitization of the peripheral zones of clastic feldspars, complete transformation of biotite flakes and formation of the microaggregates of chlorite, sericite, titanomagnetite, and rutile. Blastesis radically deformed the internal structure of the deposit long before the beginning of the greenschist stage of metamorphism.

So, the postsedimentary transformations were stronger in grainites than in sediments of the adjacent facies. Elsewhere, including the zone of catagenesis of the hostrocks, lithotypes of the deep-water grain flows were altered to the metasandstones long before the following stage of evolution of the sedimentary basin.

The second stage (period of structural reorganization of basin into a folded system) includes substages of the late metagenesis and early metamorphism displayed locally, above the centers of deep paleothermal anomalies (Yapaskurt, 1988; Yapaskurt and Andreev, 1985). Elisional processes were replaced by the diffusive metasomatic and extensive recrystallization blastic ones; consequently, cleavage structures and schistosity of rocks originated (Gusev, 1979).

The abovementioned secondary changes, as a whole, are independent of the facies. They partly inherit peculiarities of the primary composition and genesis of sediments; however, the contrast in alteration degree of rocks of different facial affiliations obviously becomes smoothed out during metamorphism.

The third stage correlated with the period of orogeny is manifested similarly as the latest regressive epigenetic changes of rocks in a Koltogor-Urengoi Graben Rift (Yapaskurt *et al.*, 1997); isolated porphyroblasts of dolomite or ankerite, which are present in deposits of all above described facies, are superposed on products of the different stages of the lithogenesis and metamorphism.

Returning to the comparative data on the lithogenesis in the basins originated in conditions of compensation filling by sediments, it should be noted that, in addition to the basin comprehensively considered in the previous work (Yapaskurt *et al.*, 1997), another basin located adjacent to the Verkhoyansk folded zone (Verkhoyansk foredeep) also deserves a special consideration, since it is a convenient intermediate link in comparison of the territorially separated basins of the Verkhoyansk region and Western Siberia. This basin has been thoroughly investigated earlier (Kossovskaya, 1962; Krashenninnikov, Yapaskurt, 1977; Yapaskurt, 1992); therefore, here it is characterized briefly.

SEDIMENTOGENESIS AND LITHOGENESIS IN THE NORTHERN SECTOR OF THE PRIVERKHROYANSK FOREDEEP

This structure is confined to the lower reaches of Lena River and has tectonic boundaries with a folded Verkhoyansk complex on the east. It is filled by a Late Jurassic to Early Cretaceous terrigenous, coal-bearing foredeep formation with greatest thickness (near the boundaries with a folded zone) of about 4.5 km. It is composed of the rocks mainly of the alluvial and marsh-lacustrine genesis. Based on the primary (sedimentogenic) features, this lithological formation is divided into essentially sandy, fluvial sediments (SF) and fine sandy to aleuropelitic, floodplain sediments (AF) facies (Figs. 6–8). Inasmuch as they are distributed within the area of coeval formations, we could delineate the longitudinal (along the strike of the present-day Lena River valley) sedimentary paleobasin, whose provenances are located on the south and southeast within the Aldan Shield and adjacent territories, as suggested by the analysis of the clastogene material composition (Kossovskaya, 1962).

Everywhere in the lowermost parts of the geological section of this complex the SF and AF facies are located in contact with shallow-marine deposits. The facies replace each other gradually, but at a rather short distances. The facies replacement started on the south; it was sufficiently younger on the extreme north (close to the present-day Lena River delta), where marine fauna is found in the lowermost formations of the Cretaceous age. To the south, marine facies are initially displaced toward the Upper Jurassic part (Sytogin and Dzhaskoi formations of the Zhigan sector of the foredeep), and then toward the Middle Jurassic part (Vilyui Syncline).

The cyclicity of facies changes is most distinctly expressed near to the areas occupied by the marine formations (on the north). It is so obvious, that by the 1930s it served as the basis for the reference stratigraphic scheme (Gusev, 1940; Glushinskii, 1973) for the Anabar–Lena and Bulun regions; the major principles of this scheme are used in the geological surveys to this day. Within the considered complex, nine formations are distinguished, some of which (the coal-bearing or contrast formations) are composed essentially of the AF and peat-bog facies with the thin SF interlayers, while the other (coal-free) formations are composed of the SF facies, i.e., coarse- to medium-grained sandy rocks of the grain flow genesis (Figs. 6, 7). In the latter rocks, the inclinations of the oblique unidirectional layer series are oriented mainly in the northern and northeast directions; this implies that most of the ancient flows were directed from the south to the north.

In a northernmost sector of the trough, where avandelta deposits are developed, G.F. Krashenninnikov assumed that estuarine sediments may be present (Yapaskurt, 1992). The thickness of sandstone formations are sharply increased in this part of the geological

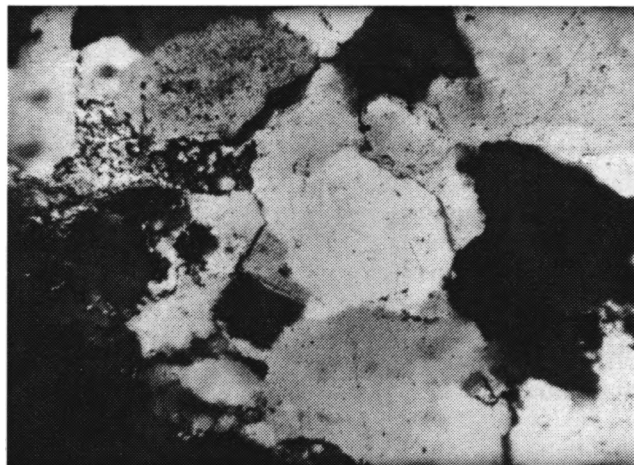


Fig. 4. Sandstone with intensely regenerated clastic quartz and gravitational corrosion textures from grain flow deposits, Sieder Formation ($C_{2,3}$), Soguru-Uel-Siktyakh River (thin section, crossed nicols, fragments are 0.2 mm across).

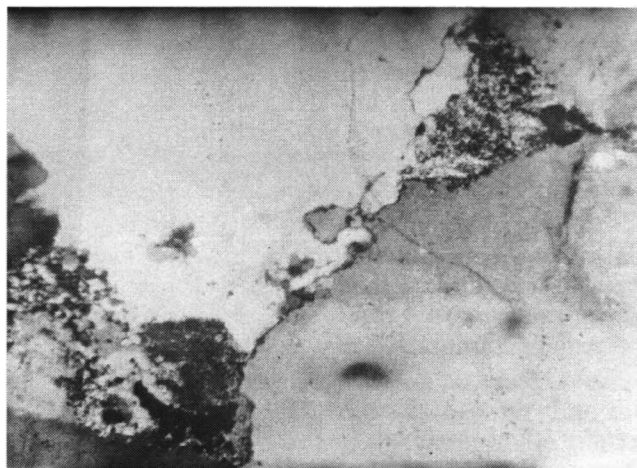


Fig. 5. Recrystallization-granulation blastesis on contacts of clastic quartz grains in sandstone of the Setachan Formation (C_2), Soguru-Uel-Siktyakh River (thin section, crossed nicols, fragments are 0.2 mm across).

section. Particularly, thicknesses of the Bakh and Lukumai formations (undivided Aptian and Albian) are 300 and 220 m, respectively; in the northwestern part, thickness of the Chonkogor Formation (Barremian) exceeds 500 m. The listed formations look monolithic in the outcrops (Fig. 7). However, on a closer examination, they consist of numerous units and lenses 0.5 to 2.5 m thick. These deposits have the steep unidirectional (Fig. 8) or intersecting oblique bedding, and sometimes an obscure horizontal-laminated structure. Sandstones in these deposits are well sorted and, as a rule, belong to the II–P variety.

We have already mentioned the prevalence of similar rocks near the fronts of certain paleodeltas. We refer to an example of Cisco System (investigated by U.E. Gallo-

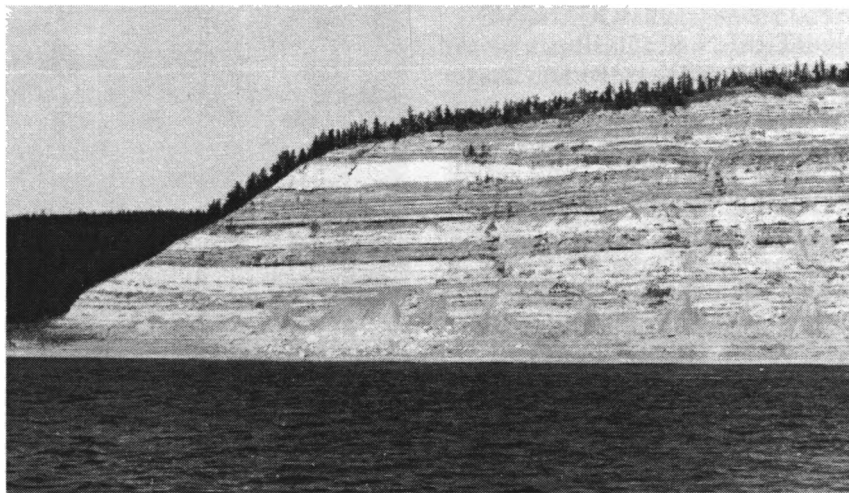


Fig. 6. Structure of one of the contrast coal-bearing formations of the Bulun Depression: cyclic alternation of the sandstones of facies SF (white), siltstones and mudstones, with coal (dark). Left bank of Lena River, 9 km downstream the mouth of Semeika River. Photo by G.F. Krashennnikov.



Fig. 7. Outcrop of the upper section of the Chonkogor sandstone formation on the left bank of Lena River, facing settlement Kyusyur. Photo by G.F. Krashennnikov.

way), formed in the Late Pennsylvanian–Permian time on the east shelf of Midland Basin, Central Texas (*Del-tas* ..., 1975). In this work, similar peculiarities of geological sections of the “major deltaic environments” and conjugated facies were illustrated by E.F. MacBrade, A.E. Vady and G.A. Wolleben for the Dyfanta Group (Upper Cretaceous–Paleocene) deposits of Parris Basin, northeastern Mexico and also by G.T. Moor and T.J. Fullam for the Pleistocene deposits of the northern and western continental margins of the Gulf of Mexico.

The mechanisms of formation of the thick sandy bodies in alluvium of the lower reaches of large rivers in the conditions of a prolonged and intensive land sub-

sidence are considered by A.A. Chistyakov *et al.* (*Strukturnaya* ..., 1983, pp. 85–86), with the recent deposits of the lower reaches of Brahmaputra River as example. Up to six facies are recognized there, in the essentially sandy alluvial deposits. One of these facies, formed in the flood channels, forms banded ridges up to 15–17 m high and 1000 m long, which are characterized by a coarse, steeply (up to 20°) cross-bedding. Another facies, also formed in a high-water stand but with detritus transportation on plain bottom, is represented by the horizontal-laminated sand units.

These and other facies can be stratified in the conditions of the fast but compensated tectonic subsidence of

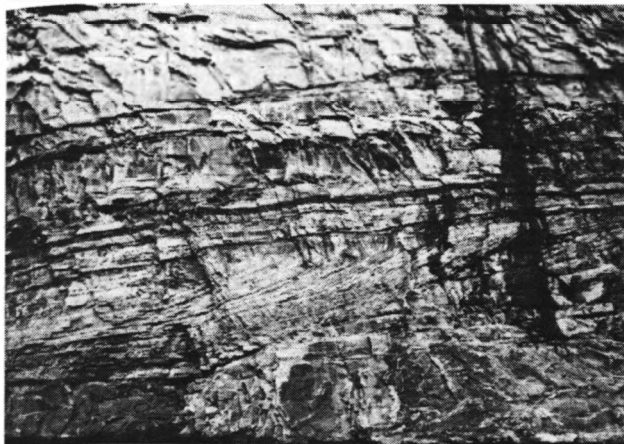


Fig. 8. Fragment of structure of the Chonkogor sandstone formation (see Fig. 7). The unidirectional oblique-laminated unit is seen at the bottom. Photo by G.F. Krashennnikov.

a substrate and united into nonuniform but thick extended bodies. The peculiarities of structure of the Lower Cretaceous sandstone formations in the Bulunskaya Depression can be explained by a similar genetic mode.

Such deposits are apparently monolithic, while actually they have a discrete internal structure favorable for the circulation of elisional fluids. Therefore, the authigenic mineral genesis in such rocks is displayed more distinctly. This process is obviously governed by the composition of sediment fund, which differed from the counterpart in the miogeosyncline formations by a steady composition, owing to a continuous support from the major feeding provenance.

As for the considered sandstones, which have a steady *average* arkosic composition, it was found out that their clastogene mineral-donors (Na–Ca-plagioclases of the andesine group, Ca-amphiboles, epidotes, garnets, etc.) served as main sources of material in the cement for the crystallization of the authigenic laumontite-group zeolites in association with corrensite, epidote, sphene, and other neoformations (Kossovskaya, 1962; Yapaskurt, 1988).

In the considered rocks the authigenic mineral genesis developed in many stages, as in the Koltogor–Urengoi Depression deposits. It allowed us, by the comparison of the genetically related lithotypes in a Mesozoic geological section of the Verkhoyansk region trough, to decipher the catagenetic and metagenetic zonation, and to prove that rocks transformations were intensified not only with increasing paleodepths of their subsidence, but also with approach of coeval sequences to the border with an adjacent folded zone (Krashennnikov and Yapaskurt, 1977; Sokolov and Yapaskurt, 1982).

CONCLUSION

The following conclusions can be made from the comparison of the paleodeltaic sediments and adjacent facies in the three regions with different tectonic modes of the sedimentary basin development.

(1) According to their landscape and climatic conditions influencing on a polymictic composition of sediment fund, deposits of the Verkhoyansk Foredeep and Koltogor–Urengoi Graben Rift have the following common features: the B/L ratio ≥ 1 , the relief of drainage systems is characterized by a primary ruggedness, the terrigenous material was transported by powerful river systems, and the sedimentation conditions approached the compensation regime.

However, their sediment funds were essentially different. For example, in the depression located within the West Siberian Plate, a vigorous subaerial basalt volcanism is marked after the Hercynian folding (Yapaskurt *et al.*, 1977). Its products have influenced the composition of clastic material in the lower part of the Triassic geological section. A major portion of the sediment fund is also represented by the products of washing of the Early Paleozoic, and partly of the diverse Precambrian magmatic and metamorphic rocks of Hercynides in the Urals and adjacent territories. In the Late Jurassic and Early Cretaceous, the Verkhoyansk Foredeep was filled by a subarkosic material, supplied mainly from the southern territories of the Aldan Shield, Sette-Daban Ridge, and Stanovoe Upland.

At the same time, alongside with mentioned distinctions, some generalities among the considered basins also became evident: first of all, it is constancy of the sediment fund composition during a prolonged period.

Contrastingly, sediment fund of an undercompensated basin in the Verkhoyansk Miogeosyncline differed by a more diverse, cyclic-changeable mineral composition (Fig. 2), because its provenances periodically underwent the tectonic reorganizations accompanied by the essential changes in their areas and peculiarities of a relief. Additionally, the presence of facies related to the redistribution of material by the high-density flows has caused more appreciable intrabasin differentiation of clastic material according to its mineral composition (for example, grainites have a less polymictic composition than sandy deposits of a delta front).

(2) According to the conditions of early lithogenesis (diagenesis), all considered sediments are rather similar. The similarity, first of all, is in incompleteness (reduction) of the diagenetic processes. At avalanche sedimentation, many of the mineral and organic components, which were in disequilibrium state and unstable in the exogenetic environment, were found to be deep-submerged soon after the deposition. Being in the intense thermobaric conditions, they represented a large reserve of material for the multistage, postdiagenetic, authigenic neoformations (for more details see Fig. 4 and its interpretation in Yapaskurt *et al.*, 1997).

Therefore, most of the rocks bear only traces of the diagenetic stage.

(3) At the stage of catagenesis (during deep submergence of sedimentary complexes) the authigenic mineral genesis depends first of all on a sediment fund composition. At the same time, in basins with undercompensated filling by sediments, this dependence is not everywhere direct. It almost disappears along with the complications in the facial series structure and the changes in quantitative proportions between sandy and aleuropelitic sediments.

In the miogeosynclinal complex, aleuropelitic sediments prevail over the sandy ones, especially along the periphery of the underwater alluvial fans. This phenomenon had a strong influence on activation of the elisional catagenetic processes. In particular, the intense fluid inflow into the grainite layers caused an "advancing" rate of their mineral and structural changes in comparison with the surrounding aleuropelitic sediments (grainites acquired the metarock appearance long before the stage of initial metamorphism).

Hence, intensity of the elisional processes of catagenesis is governed by the facial features as well as tectonic modes in the sedimentary basins.

(4) For the same reason, in the miogeosyncline environment, the deltaic deposits and adjacent facies underwent the strongest, multistage, postcatagenetic alterations of their composition, texture, and structure.

All the aforesaid should be taken into account at the stage-by-stage reconstructions of the initial composition of sedimentary complexes and interpretation of the peculiarities of paleotectonic evolution of ancient sedimentary basins.

ACKNOWLEDGMENTS

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Geochemistry of Rare Earth Elements in Nodules and Host Sediments in the Northern Equatorial Pacific

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Abstract—The paper discusses the behavior of rare earth elements (REE) in nodules and host sediments at ten stations located along a sublateral profile within the Clarion–Clipperton Province. The composition and content of REE in sediments (except Ce) are determined by their content in phosphate (bony apatite and iron hydroxophosphates). Rare earth elements in the radiolarian zone nodules are mainly related to iron oxyhydroxides and hydroxophosphates. The relationship between these phases governs the value of Ce anomaly in the REE composition of nodules. The ratio $Ce/Ce^* > 1$ is typical of sedimentary nodules, while $Ce/Ce^* \leq 1$ is observed in diagenetic and sedimentary diagenetic varieties. We propose a nodule formation model that elucidates the local variability of the radiolarian zone nodules.

INTRODUCTION

The northern equatorial Pacific, which is located between the Clarion and Clipperton fracture zones, has drawn the attention of researchers due to an extensive development of ferromanganese nodules (FMN) with abundant Cu, Ni, and Co (Calvert *et al.*, 1978, 1987; Calvert and Piper, 1984; Glasby *et al.*, 1987; Piper, 1988; Skornyakova, 1986). Nodules developed in siliceous muds over minor areas of the seafloor are characterized by a strong variability of their composition. Based on the Mn/Fe ratio, they can be divided into sedimentary (S), diagenetic (D), and sedimentary diagenetic (SD) types with Mn/Fe values equal to <2.5 , >4 , and 2.5 – 4 , respectively (Skornyakova, 1986; Uspenskaya and Skornyakova, 1991). Sedimentary and diagenetic nodules significantly differ from each other in their mineral and chemical compositions. Sedimentary nodules are composed of major vernadite (δ -MnO₂) and enriched in Fe, Ti, Co, as well as Ce and other REE. Diagenetic nodules are composed of predominant buserite and enriched in Mn, Cu, Ni, and Mo. Sedimentary diagenetic nodules occupy an intermediate position.

All the aforesaid nodule types have an asymmetric chemical composition; the upper section of nodules is always enriched in Fe, Co, Th, and REE, whereas the lower section is enriched in Mn, Ni, Cu, and, occasionally, Co and Mo (Dymond *et al.*, 1984; Elderfield *et al.*, 1981b; Skornyakova, 1986). This can be explained by the unequal contribution of various sources of material. Presumably, the upper section was more often subjected to the influence of direct precipitation of suspension (iron and manganese oxyhydroxides), whereas the

lower section was a product mostly of diagenetic remobilization of the reactive part of sediments. The remobilization is promoted by a high bioproductivity of surface waters.

According to Skornyakova, the local compositional variability of the radiolarian zone nodules is related to near-bottom conditions, i.e., the position of seafloor relative to the carbonate compensation depth and the influence of near-bottom currents (Skornyakova and Murdmaa, 1986). The change of thickness and even complete disappearance of Quaternary sediments on the seafloor, as well as the assignment of sedimentary nodules to ridges and slopes of abyssal hills, are evidence of an intense rewashing of sedimentary material (Sval'nov, 1986).

The REE signature in the radiolarian zone nodules was studied at separate sites; in some cases, rare earth elements were represented only by La and Ce (Elderfield *et al.*, 1981a; Calvert and Piper, 1984; Calvert *et al.*, 1987; Korsakov, 1992). At DOMES Site A (Fig. 1), it was found that the REE composition in nodules depends upon the nodule type (S, SD, and D); the significant positive anomaly of Ce is noted only in the S-type nodules or abyssal hill nodules (Calvert *et al.*, 1987).

The simultaneous study of the REE behavior in nodules and host rocks at the WAHINE Site (Elderfield *et al.*, 1981a) made it possible to elucidate specific features of the REE composition in nodules and sediments. Rare earth elements (except Ce) in the radiolarian zone sediments are related to the P-phase; the REE composition in nodules is governed by the ratio of REE in the P- and Fe-phases (iron oxyhydroxides); Ce in nodules is generally linked to Fe; the REE distribution in nodules is asymmetrical: relative to the lower sections, the upper sections are more enriched in REE, especially Ce (Elderfield *et al.*, 1981b).

[†] Deceased.

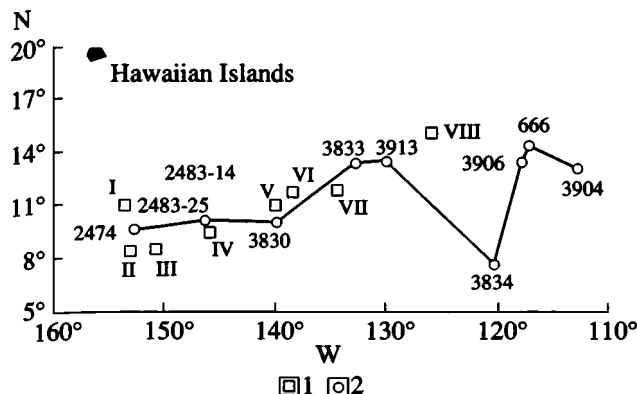


Fig. 1. Map of the study area. (1) Stations of the profile; (2) sites: (I) 5996, (II) WAHINE, (III) DOMES-A, (IV) Valdivia-13/2; (V) MANOP Site S; (VI) DOMES-B; (VII) Site C; (VIII) DOMES-C.

The objective of this work was to study the REE behavior in nodules and host rocks at ten stations located along the sublateral (10°N) profile within the Clarion-Clipperton Province of the Pacific (Fig. 1), investigate the variation of REE composition in nodules and sediments within the radiolarian zone, and elucidate the nature of these variations and possible connections of the nodule composition with host sediments and their reactive part.

MATERIALS AND METHODS

As is evident from Fig. 1, this work is based on samples collected during cruises of the R/V *Dmitrii Mendeleev* (Leg 28: stations 2474 and 2483; Leg 41: stations 3830, 3833, 3834, 3904, and 3906) and the R/V *Akademik Mstislav Keldysh* (Leg 6: Station 666). The studied sediments represent clayey-radiolarian oozes enriched in diatoms to a variable extent. Only sediments from Station 3834 are composed of coccolith-foraminiferal carbonate muds with a radiolarian admixture.

Bulk samples of sediments (50 mg) and nodules (30 mg) were treated with a HF and HClO₄ mixture in platinum bowls. The manganese oxide precipitate formed as a result of the nodule decomposition was reduced in 10 ml of 6 M HCl. Then samples were converted into a 5% HNO₃ solution and used for the analysis of REE, Th, W, and Mo with the application of the mass spectrometry with induction connected plasma (ICP-MS) method (Dubinin, 1993; Strekopytov and Dubinin, 1996). In order to determine the composition of the reactive part of sediments, samples were treated with 1 M NH₂OH · HCl + 25% CH₃COOH solution at room temperature under periodic shaking for 4 h (Chester and Hughes, 1967; Dubinin and Strekopytov, 1994). After filtration through a paper filter (pore size 1–2 μm), hydroxylamine was decomposed by concentrated nitric acid under heating and then samples were transferred into 5% HNO₃ solution for the subsequent

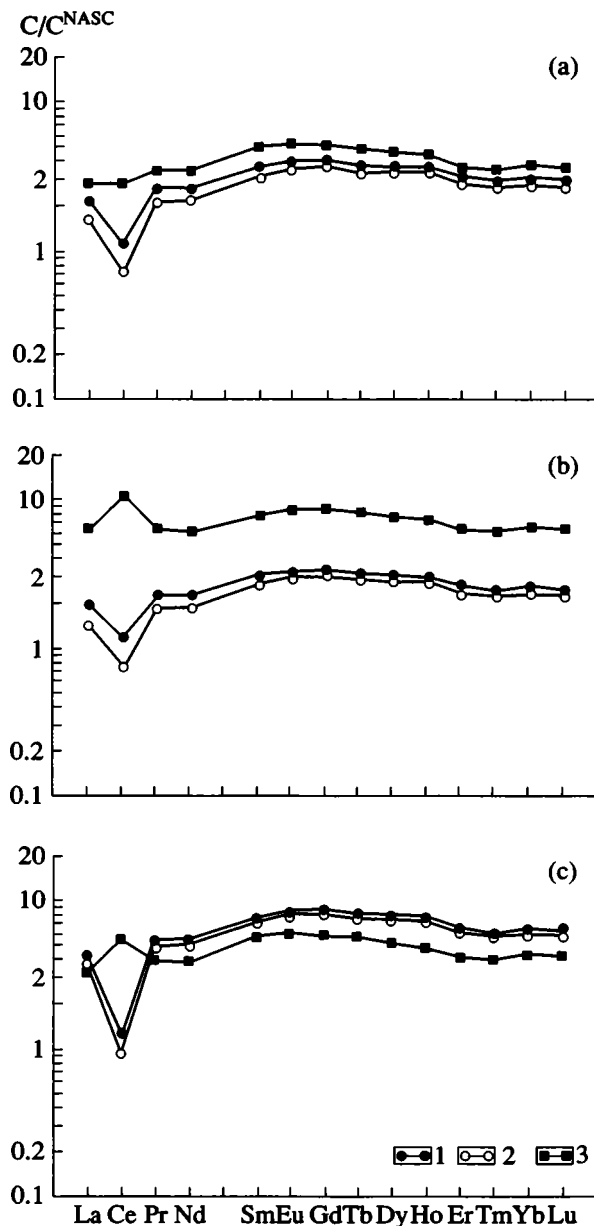


Fig. 2. NASC-normalized (Gromet *et al.*, 1984) compositions of REE. (1) Sediments, (2) reactive part of sediments, (3) nodules. Stations: (a) 2483-14, (b) 2483-25, (c) 3830-19.

analytical procedure. Fe, Mn, Al, and Ti were analyzed by the flame atomic absorption method (N.N. Zavadskaya, analyst). Additionally, nodules were examined for the concentration of Co, Ni, and Cu with an accuracy of 3–5 rel. %. Phosphorus was determined by the spectrophotometric study of color intensity of the blue P-Mo-Sb complex (Unifitsirovannye ..., 1971).

RESULTS

Results of the analysis of sediments from ten stations along the profile are given in Table 1. Data on the

Table 1. Element contents in sediments of the profile

Element	Stations									
	2474-24	2483-14	2483-25	3830-19	3833-24	3913-3	3834-1	3906-3	666	3904-1
La	46.3	69.3	62.5	137	53.6	36.8	20.3	54.4	47.3	57.0
Ce	82.4	82.8	87.4	93.1	87.5	81.2	17.3	97.8	80.4	79.0
Pr	13.4	21.0	18.4	42.3	16.2	10.5	5.63	16.2	13.7	16.3
Nd	54.6	88.4	77.2	180	67.4	41.9	24.3	68.1	57.4	67.9
Sm	12.9	21.2	18.6	43.6	16.2	9.82	5.83	16.3	13.8	16.5
Eu	2.83	5.05	4.28	10.3	3.71	2.16	1.36	3.76	3.04	4.05
Gd	12.8	21.7	18.6	44.9	16.2	9.33	6.27	16.1	13.6	16.6
Tb	1.92	3.28	2.86	6.87	2.47	1.43	0.95	2.44	2.07	2.50
Dy	11.6	19.9	17.2	41.0	14.6	8.44	5.86	14.3	12.2	14.9
Ho	2.24	3.91	3.34	7.97	2.86	1.58	1.16	2.74	2.29	2.98
Er	6.38	11.1	9.50	21.9	7.96	4.67	3.45	7.66	6.69	8.32
Tm	0.89	1.54	1.31	2.94	1.12	0.64	0.48	1.05	0.92	1.23
Yb	5.72	10.0	8.68	19.5	7.47	4.28	3.08	7.03	6.02	7.88
Lu	0.86	1.49	1.26	2.90	1.11	0.65	0.47	1.05	0.91	1.16
Th	10.0	11.9	11.6	11.2	12.9	10.0	2.0	10.0	9.2	9.3
Mo	3.6	3.5	6.3	18.2	5.0	5.8	1.6	52.6	11.4	13.8
W	6.4	5.3	5.8	4.9	5.7	6.6	1.8	9.6	6.7	7.4
Mn	0.43	0.37	0.52	0.61	0.37	0.45	0.28	2.83	0.94	1.46
Fe	4.15	3.93	4.34	4.06	4.17	3.87	1.14	4.62	4.64	4.66
Al	6.60	6.20	6.63	6.63	6.99	6.70	1.32	6.20	6.42	6.53
Ti	0.33	0.30	0.30	0.31	0.32	0.30	0.02	0.32	0.26	0.28
P	0.11	0.267	0.20	0.389	0.13	0.092	0.049	0.119	0.110	0.184
C _{org}	0.40	0.45	0.37	0.33	0.31	0.35	0.30	0.41	0.49	0.64
CaCO ₃	1	1	n. d.	1.7	n. d.	n. d.	73.3	1	—	1.4
Ce/Ce*	0.73	0.47	0.56	0.26	0.64	0.92	0.35	0.71	0.68	0.56

Note: REE, Th, Mo, and W are given in ppm, other elements are in %.

$Ce/Ce^* = 2 \times (Ce/Ce^{NASC}) / (La/La^{NASC} + Nd/Nd^{NASC})$, (n. d.) not detected.

C_{org} and CaCO₃ contents were supplied by V.N. Sval'nov. The NASC-normalized REE compositions (Gromet *et al.*, 1984) in nodules and host sediments, as well as their reactive part in sediments from three representative stations, are shown in Fig. 2. The REE composition in sediments is marked by a negative Ce anomaly and relative maximum in the intermediate REE domain.

Based on the correlation data (Table 2), one can distinguish three groups of elements: Fe–Ti–Al–Ce–Th–W, Mn–Mo–W, and REE(III)–P. Evidently, the first group is a member of the aluminosilicate matrix and iron oxyhydroxides, the second group is incorporated in manganese oxyhydroxides, and the third group is an indicator of the association of trivalent REE with phosphates. This inference is in agreement with data obtained only for the WAHINE Site (Elderfield *et al.*, 1981a). Phosphorus practically governs the content of REE in sediments, except La, and the regression lines approach zero when the phosphorus content is equal to zero (Fig. 3).

In order to examine the influence of composition of the reactive part of host sediments upon the nodule composition, sediments were treated with the Chester reactive. It is known (Chester and Hughes, 1967; Dubinin and Strekopytov, 1994) that this reactive is able to extract all manganese oxyhydroxides and 90% low-crystallized iron oxyhydroxides, as well as to dissolve the whole bony apatite of even the silt-size fraction without affecting the sediment's aluminosilicate component. With this fact in mind, let us examine data on the element content in extracts (Table 3 and Fig. 4): 87–97% Mn and only 7–11% Al pass into the extract; Ti could not be determined, because its content is <0.01%; the Fe extraction is as much as 16–26% in sediments from four eastern (nearest to EPR) stations and only 5–8% at other stations of the study profile.

The Bostrom criterion, Al/(Al + Fe + Mn) value, of the presence of hydrothermal material (Bostrom, 1973) is <0.4 in sediments from all stations. The contents of reactive and total Fe are almost equal in metalliferous sediments of the EPR (Dubinin and Volkov, 1992).

Table 2. Coefficients of correlation between element contents in sediments of the profile, n = 10, P = 0.95, r = 0.63

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	Mo	W	Mn	Fe	Al	Ti	P
La	1.00	0.53	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.51	0.21	0.05	0.01	0.36	0.43	0.45	0.95
Ce		1.00	0.53	0.51	0.51	0.49	0.48	0.48	0.47	0.46	0.47	0.47	0.48	0.47	0.91	0.43	0.77	0.36	0.93	0.95	0.97	0.46
Pr			1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.51	0.21	0.04	0.00	0.35	0.42	0.44	0.95
Nd				1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.49	0.21	0.03	0.01	0.33	0.40	0.42	0.95
Sm					1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.49	0.21	0.03	0.01	0.33	0.40	0.42	0.95
Eu						1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.48	0.21	0.02	0.01	0.32	0.38	0.40	0.96
Gd							1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.47	0.20	0.00	-0.01	0.31	0.37	0.39	0.95
Tb								1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.47	0.20	0.00	-0.01	0.31	0.37	0.39	0.95
Dy									1.00	1.00	1.00	1.00	1.00	1.00	0.46	0.18	-0.02	-0.02	0.30	0.36	0.38	0.96
Ho										1.00	1.00	1.00	1.00	1.00	0.46	0.18	-0.02	-0.02	0.29	0.36	0.38	0.96
Er											1.00	1.00	1.00	1.00	0.46	0.17	-0.03	-0.03	0.29	0.36	0.38	0.96
Tm												1.00	1.00	1.00	0.48	0.17	-0.01	-0.02	0.31	0.37	0.39	0.97
Yb													1.00	1.00	0.48	0.18	-0.01	-0.02	0.31	0.37	0.39	0.97
Lu														1.00	0.47	0.17	-0.02	-0.02	0.30	0.37	0.38	0.96
Th															1.00	0.10	0.53	0.03	0.82	0.93	0.93	0.50
Mo																1.00	0.69	0.94	0.38	0.17	0.27	0.07
W																	1.00	0.77	0.84	0.70	0.73	-0.03
Mn																		1.00	0.43	0.16	0.23	-0.08
Fe																			1.00	0.94	0.91	0.31
Al																				1.00	0.97	0.38
Ti																					1.00	0.39
P																						1.00

Note: (n) number of samples, (r) correlation coefficient significant at confidence level (P).

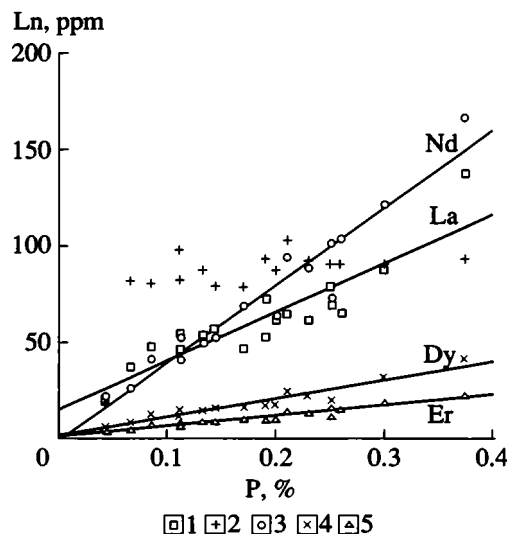


Fig. 3. REE vs. P in sediments of the profile. Supplemented with data from (Elderfield *et al.*, 1981a) for WAHINE Site. (1) La; (2) Ce; (3) Nd; (4) Dy; (5) Er.

With an eye to increased values of Fe_{react}/Fe_{tot} (relative to normal pelagic muds) in sediments from four eastern stations and their geographic proximity to the EPR, we can assume the presence of hydrothermal material in the aforesaid sediments (Fig. 4). The extraction of phosphorus from sediments is 100% in the western sector of the profile and only 70–93% in the eastern sector. Obviously, a part of phosphorus in sediments from the eastern sector is connected with iron oxyhydroxides, as is common in hydrothermal iron oxyhydroxides (Berner, 1973), and their incomplete transition into extract decreases the share of phosphorus in solution.

The analysis of data on the content of elements in extracts and the total content of elements in sediments revealed the following distinct correlations: Fe–Mn, Al–Ce, Mn–Mo, and P–REE–Th–W–Ce. The Fe–Mn correlation suggests that mostly iron oxyhydroxides are transferred to the extract fraction. The REE–P correlation is stronger in extracts than in bulk samples due to the separation of REE connected with the aluminosilicate matrix of sediments. The Ce–P correlation is registered, but its considerably less inclined regression slope differs from the REE–P counterpart and does not approach zero (Fig. 5). Tungsten is probably connected with lithogenic material to a greater extent than Mo, as is evident from the data on extracts; the extraction degree is up to 11–36% (63% in one case) for W and as much as 60–100% for Mo. The Th content in the extract fraction accounts for 5–10% of its total content; in our opinion, this is related to the Th resorption by sediment from the extract.

The element concentrations in nodules are given in Table 4. Based on the Mn/Fe value, the majority (8 out of 10) of the nodules belong to the D-type; this does not reflect the real distribution of nodules of this type in the

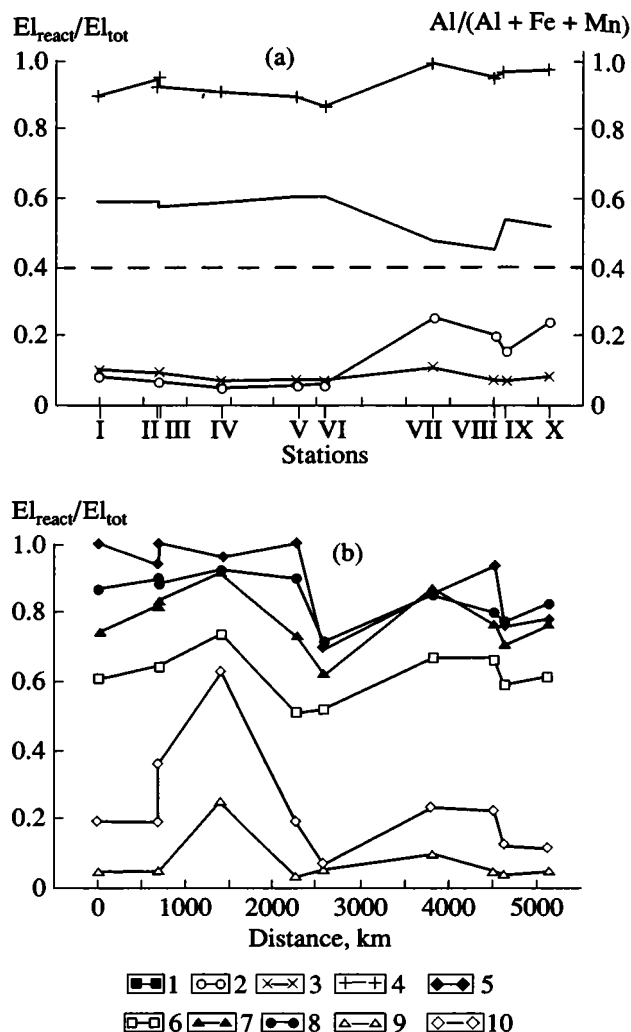


Fig. 4. (a) Distribution of $Al/(Al + Fe + Mn)$ and (b) relative element contents (El_{react}/El_{tot}) in the reactive part of sediments of the profile.

(1) $Al/(Al + Fe + Mn)$, (2) Fe, (3) Al; (4) Mn; (5) P; (6) Ce; (7) Nd; (8) Er; (9) Th; (10) W. Stations of the profile: (I) 2474; (II) 2483-25; (III) 2483-14; (IV) 3830; (V) 3833; (VI) 3913; (VII) 3834; (VIII) 3906; (IX) 666; (X) 3904.

radiolarian belt (Skornyakova, 1986). The local variability of nodules is exemplified by two stations at Site 2483 (Fig. 2). The compositions of sediments and their reactive parts (except P) are virtually similar, but the nodule compositions strongly differ: the Station 2483-14 nodule may be identified as the D-type ($Mn/Fe = 5.2$, $Ce/Ce^* = 0.90$), whereas the Station 2483-25 nodule belongs to the S-type ($Mn/Fe = 1.3$, $Ce/Ce^* = 1.7$). Station 2483-14 is located in a trough, while Station 2483-25 is situated on a hilltop. The REE content is higher in nodules than in sediments at all studied stations, except Station 3830 where the content of P in sediment may be as much as 0.39% (Fig. 2).

The analysis of the entire sample set of nodules reveals the conventional correlations Fe–REE(+Ce)–Ti

and Mn–Ni–Mo–Cu, as well as the nonconventional correlations P–W, W–Dy...Lu, and Th–Ce...Tb–Ti–Co. However, several correlations were produced by the inclusion of two hydrogenous nodules from stations 2474 and 2483-25 into the sample set. If these nodules are excluded, the Fe–REE, Mn–Ni, and Cu–Mo correlations disappear.

DISCUSSION

The collection of abundant documentary material from various sites of the Pacific radiolarian zone made it possible to study a series of regularities that are typical of both separate sites and the radiolarian zone in general. The objective of our work was to reveal common features of the REE behavior in sediments and radiolarian zone nodules and extrapolate the previously discovered regularities over the entire silica accumulation zone in the equatorial Pacific.

So far, only one has been devoted to the examination of the correlation of REE compositions in nodules and host sediments of the radiolarian zone. Elderfield *et al.* (1981a) demonstrated that rare earth elements in sediments are associated with phosphorus (P-phase). They assumed that the REE compositions in the P-phase and biogenic bony apatite are identical. Our studies revealed that the P-phase is completely dissolved on treatment of sediments with the Chester reactive and the REE–P correlation is refined (Figs. 3, 5). Under this technique of separating the reactive part of sediment, the bony apatite is completely dissolved (Dubinin and Strekopytov, 1994); hence, it is possible to assume the compositional identity of bony apatite and P-phase.

Taking into consideration the elevated bioproductivity ($100\text{--}500\text{ mg C}_{\text{org}}/(\text{m}^2\text{ day})$) of surface waters (Murdmaa, 1986) and low sedimentation rates ($1\text{--}3\text{ mm/ka}$), one can expect the accumulation of bony phosphate in the radiolarian zone sediments. Let us examine the potential REE(III) accumulation in bony apatite in the REE/P ratio (in g/g) version. The REE content in bony phosphate depends upon a number of factors: sedimentation rate, porosity, and phosphate fragment dimension. Based on extract data, average individual REE/P ratios in the radiolarian zone sediments range from 0.004 for Nd/P to 0.00007 for Tm/P and Lu/P, which are similar to ranges for Nd/P (0.002) and Tm/P and Lu/P (0.00004) in bony apatite from the South Pacific Basin (our unpublished data).

According to Elderfield and Pagett (1986), the Nd/P value in bony phosphate from the Pacific pelagic muds ranges from 0.0007 to 0.002. Similar values are also encountered in the Oligocene–Lower Miocene Maikop sediments, in which the pure phosphate-based Nd/P and Tm/P values are equal to 0.004 and 0.000076, respectively (Stolyarov *et al.*, 1991). The Ce pattern cannot be explained by its dependence on phosphorus content in sediments (Fig. 3). Such a relationship is observed only in extracts (Fig. 5). The P-independent

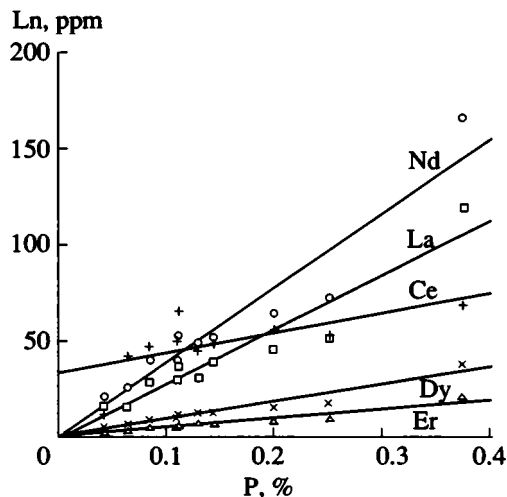


Fig. 5. REE vs. P in the reactive part of sediments of the profile. Legend as in Fig. 3.

(distinct from zero) member in the regression equation $[\text{Ce}] = 0.0104[\text{P}] + 33$ may suggest the contribution of another source, e.g., iron oxyhydroxides, to the Ce content. Based on extract data, the average content of reactive Fe in sediments is equal to 0.47% (Table 3), and the $\text{Ce}_{\text{react}}/\text{Fe}_{\text{react}}$ value is 0.007. Similar values of the specific concentration of REE(III) in phosphate are also typical of various types of pelagic sediments. A strong REE–P correlation is registered in several samples of the Pacific pelagic sediments (Toyoda *et al.*, 1990; Strekopytov, 1996).

In general, rare earth elements in the studied nodules are connected with iron oxyhydroxides, although, according to our data, significant coefficients of correlation between Fe and REE are related to the presence of two hydrogenous nodules in the sample set of diagenetic nodules. As was previously demonstrated for moderate-size radiolarian sites (Fig. 6), rare earth elements, including Ce, in nodules are generally associated with iron oxyhydroxides (Elderfield *et al.*, 1981a; Calvert and Piper, 1984). Elderfield *et al.* (1981a) attributed the Ce anomaly variation in nodules to the connection of trivalent REE with iron oxyhydroxides and P-phase, which is analogous to the P-phase in host sediments. Therefore, the content of trivalent REE associated with iron oxyhydroxides can be found by the deduction of REE associated with the P-phase in the reactive part of sediments, according to the following formula: $\text{REE} = \text{REE}_{\text{nod}} - \text{P}_{\text{nod}}(\text{REE}_{\text{react}}/\text{P}_{\text{react}})$, where indices “nod” and “react” denote the element concentration in nodules and reactive part of sediments, respectively. The correction for lithogenic Fe can be introduced on the basis of Al, considering that the whole of Al is lithogenic:

$$\text{Fe} = \text{Fe}_{\text{nod}} - \text{Al}_{\text{nod}} \times ((\text{Fe}_{\text{sed}} - \text{Fe}_{\text{react}})/(\text{Al}_{\text{sed}} - \text{Al}_{\text{react}})),$$

Table 3. Element contents in the reactive part of sediments of the profile

Element	Stations									
	2474-24	2483-14	2483-25	3830-19	3833-24	3913-3	3834-1	3906-3	666	3904-1
La	29.3	52.0	45.6	120	31.4	16.7	16.3	36.9	28.8	38.9
Ce	50.0	53.2	55.7	68.9	44.8	42.2	11.6	65.3	47.6	48.6
Pr	9.68	16.9	14.9	38.3	11.2	6.20	4.81	12.2	9.55	12.2
Nd	40.6	72.6	64.3	166	49.5	26.1	21.2	52.4	40.8	52.0
Sm	10.4	18.2	16.1	40.5	12.7	6.82	5.04	13.2	10.2	12.6
Eu	2.60	4.51	3.97	9.96	3.17	1.71	1.28	3.10	2.53	3.09
Gd	11.1	19.5	16.8	42.5	14.1	7.23	5.42	13.6	11.2	13.8
Tb	1.70	2.92	2.61	6.41	2.14	1.11	0.80	2.05	1.67	2.09
Dy	10.4	18.0	15.4	38.3	12.8	6.42	5.00	11.8	9.72	12.6
Ho	1.97	3.54	3.07	7.40	2.50	1.22	1.00	2.26	1.89	2.46
Er	5.54	9.92	8.39	20.3	7.20	3.34	2.95	6.13	5.19	6.89
Tm	0.78	1.37	1.19	2.81	1.06	0.48	0.40	0.88	0.70	0.95
Yb	5.03	8.88	7.54	17.9	6.32	3.13	2.65	5.61	4.78	6.16
Lu	0.72	1.31	1.15	2.68	1.03	0.47	0.39	0.81	0.70	0.92
Th	0.5	0.6	0.5	2.8	0.5	0.5	0.2	0.5	0.4	0.5
Mo	2.9	2.8	5.4	16.5	3.7	3.5	1.6	40.1	7.9	10.0
W	1.2	1.0	2.1	3.1	1.1	0.5	0.4	2.2	0.8	0.8
Mn	0.39	0.35	0.48	0.55	0.33	0.39	0.28	2.68	0.91	1.42
Fe	0.35	0.28	0.29	0.21	0.25	0.23	0.29	0.95	0.73	1.12
Al	0.68	0.58	0.61	0.47	0.51	0.48	0.14	0.45	0.46	0.54
P	0.11	0.251	0.20	0.374	0.13	0.064	0.042	0.111	0.084	0.143
Ce/Ce*	0.64	0.38	0.45	0.22	0.49	0.88	0.28	0.65	0.61	0.48
Mn/Fe	1.1	1.2	1.7	2.6	1.3	1.7	1.0	2.8	1.2	1.3

Note: REE, Th, Mo, and W are given in ppm, other elements are in %.

where indices "nod," "sed," and "react" denote the element content in nodules, sediments, and their reactive part, respectively. The Fe-REE(III) correlation is not refined after recalculation, although correlation coefficients remain significant (Fig. 7). The recalculation upgraded correlation in the case of moderate-size radiolarian sites (Calvert *et al.*, 1978; Elderfield, *et al.*, 1981a).

The weak Ce-P correlation in the reactive part of sediments indicates that Ce is associated with iron oxyhydroxides. Different modes of trivalent REE and Ce occurrence may be linked to the higher oxidation degree of cerium (Ce⁴⁺). The Ce/Fe values in the reactive part of sediments and nodules are very close (0.007 and 0.008, respectively). The preferential association of Ce in sediments and nodules with iron oxyhydroxides and the association of trivalent REE in sediments and, partially, nodules with phosphorus are responsible for the origination of negative Ce anomaly in diagenetic nodules and positive Ce anomaly in sedimentary varieties (Fig. 8).

As is evident from Tables 3 and 4, phosphorus is more accumulated in nodules than in the reactive part of host sediments. The comparison of phosphorus content in these two media reveals that the $P_{\text{nod}}/P_{\text{react}}$ value is <1 only in two cases out of ten: it is close to 1 (0.96) in the hydrogenic nodule from Station 2483-25 and equal to 0.52 in the sediment from Station 3830; in the latter case, the REE concentrations are higher in host sediments than in nodules (Fig. 2). The higher accumulation of phosphorus in nodules relative to sediments suggests that bony apatite is not a dominant form of phosphorus in sediments.

The analysis of phosphorus and iron content in the radiolarian zone nodules on the basis of data of Calvert *et al.* (1978, 1987), Elderfield *et al.* (1981a), Calvert and Piper (1984) and our data revealed a positive correlation between these elements (Fig. 9). A considerable amount of phosphorus may be present in seven nodules among the examined 111 radiolarian zone samples (increased Ca is noted in three samples). The presence of a direct correlation between P and Fe in nodules (Fig. 9) suggests that phosphorus is associated with

Table 4. Element contents in nodules of the profile

Element	Stations									
	2474-24	2483-14	2483-25	3830-19	3833-24	3913-3	3834-1	3906-3	666	3904-1
La	182	90.5	208	104	78.4	94.3	104	115	93.2	102
Ce	960	208	801	395	173	310	133	277	238	222
Pr	49.7	27.6	52.3	31.8	23.7	32.1	27.1	34.2	27.8	28.9
Nd	196	115	211	128	98.5	132	116	140	117	118
Sm	45.8	28.8	47.4	31.9	24.3	34.4	26.4	33.8	28.2	29.0
Eu	10.8	6.68	11.3	7.30	5.55	8.11	6.45	7.81	6.49	6.54
Gd	43.7	27.5	47.6	29.7	22.5	31.0	26.9	33.0	26.7	28.5
Tb	6.76	4.23	7.46	4.69	3.43	4.83	4.09	4.94	4.18	4.29
Dy	38.8	25.1	42.6	26.5	19.3	26.8	24.3	28.1	23.4	25.5
Ho	7.11	4.68	8.10	4.87	3.57	4.71	4.74	5.27	4.32	4.77
Er	19.1	12.8	22.8	13.7	9.78	12.7	13.2	14.7	11.7	13.5
Tm	2.76	1.83	3.31	1.96	1.38	1.84	1.87	2.05	1.77	1.91
Yb	18.2	12.1	21.9	13.1	8.86	12.4	12.6	13.8	11.6	13.0
Lu	2.66	1.78	3.25	1.93	1.34	1.83	1.84	2.01	1.70	1.94
Th	28.2	17.3	18.6	17.3	10.7	23.6	5.43	13.0	12.2	10.3
Mo	282	418	316	564	496	575	454	573	602	560
W	85.7	166	208	54.2	48.7	54.6	63.6	53.1	45.9	37.6
Mn	21.3	23.9	17.9	25.9	26.7	28.4	29.8	27.9	29.6	26.6
Fe	10.9	4.55	14.0	6.17	5.36	4.57	6.79	5.14	5.40	6.30
Al	1.25	2.77	2.19	2.24	2.28	2.21	1.71	2.17	2.08	2.18
Ti	0.97	0.34	0.77	0.43	0.15	0.27	0.16	0.22	0.22	0.25
Co	0.33	0.23	0.18	0.23	0.24	0.18	0.12	0.16	0.13	0.10
Ni	0.49	1.29	0.41	1.10	1.18	1.45	1.16	1.18	1.22	1.21
Cu	0.37	0.98	0.27	0.79	1.26	1.21	0.88	1.05	1.03	1.09
P	0.175	0.318	0.191	0.194	0.146	0.124	0.168	0.155	0.145	0.155
Ce/Ce*	2.27	0.90	1.70	1.52	0.87	1.22	0.54	0.97	1.01	0.90
Mn/Fe	1.96	5.26	1.27	4.20	4.99	6.22	4.38	5.42	5.48	4.22

Note: REE, Th, Mo, and W are given in ppm; other elements are in %.

iron oxyhydroxides in the phosphate form; i.e., it is present as iron hydroxophosphates. The average mole ratio of P/Fe is 0.018 for the radiolarian zone nodules.

The phosphate sorption from oceanic water by newly formed suspended particles of hydrothermal iron oxyhydroxides elevates the aforesaid mole ratio up to 0.20. The process of sorption depends upon the concentration of phosphates dissolved in oceanic water (Feely *et al.*, 1991). This conclusion is in agreement with the experimental model of phosphorus coprecipitation by iron oxyhydroxides during the interaction between hydrothermal solution and sea water. Under the approximation of experimental conditions to natural ones, the mole ratio of P/Fe in the newly formed solid phase tends to 0.25 (Savenko, 1995). The presence of hydrothermal material in the form of iron and manganese

oxyhydroxides in metalliferous sediments results in close correlation between P and Fe (Berner, 1973).

The extraction of P in the phosphate variety from oceanic water is typical not only for hydrothermal iron oxyhydroxides. Phosphorus is abundant in interlayers of diagenetic iron oxyhydroxides and shallow-water nodules (Calvert and Price, 1977; Volkov and Yagodin-skaya, 1979). The sequential extract data indicate that more than half of phosphorus reserves in hydrogenic crusts on the Pacific seamounts are associated with iron oxyhydroxides (Koschinsky and Halbach, 1995).

The experimental investigation of the phosphate ion adsorption on the surface of iron and manganese oxyhydroxides showed that at pH $\approx$ 8, 0.1 M concentration of KCl solution, equivalent concentration of free adsorption centers on oxyhydroxide surfaces, and P concentration equal to 4.8 μ mol/l, more than 90% P is

Table 5. Coefficients of correlation between element contents in nodules of the profile, $n = 10$, $P = 0.95$, $r = 0.63$

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Mn	Fe	Al	Ti	Co	Ni	Cu	P	Th	Mo	W
La	1.00	0.92	0.98	0.98	0.94	0.95	0.98	0.97	0.98	0.99	0.98	0.99	0.98	0.98	-0.84	0.96	-0.47	0.89	0.32	-0.95	-0.94	0.04	0.51	-0.78	0.61
Ce		1.00	0.96	0.95	0.95	0.94	0.93	0.94	0.93	0.90	0.88	0.89	0.87	0.87	-0.82	0.86	-0.53	0.98	0.60	-0.91	-0.89	0.03	0.75	-0.75	0.47
Pr			1.00	1.00	0.99	0.99	1.00	1.00	0.99	0.98	0.97	0.97	0.96	0.96	-0.82	0.90	-0.46	0.92	0.41	-0.90	-0.90	0.02	0.67	-0.72	0.57
Nd				1.00	0.99	0.99	1.00	1.00	0.99	0.98	0.97	0.98	0.97	0.97	-0.82	0.90	-0.45	0.91	0.38	-0.90	-0.90	0.02	0.64	-0.73	0.59
Sm					1.00	1.00	0.99	0.99	0.98	0.96	0.94	0.94	0.94	0.94	-0.80	0.84	-0.42	0.91	0.43	-0.84	-0.85	0.01	0.74	-0.67	0.55
Eu						1.00	0.99	0.99	0.98	0.96	0.95	0.95	0.95	0.94	-0.79	0.85	-0.44	0.91	0.42	-0.84	-0.86	0.01	0.72	-0.70	0.57
Gd							1.00	1.00	1.00	0.99	0.98	0.98	0.98	0.98	-0.82	0.89	-0.42	0.90	0.35	-0.88	-0.89	0.03	0.64	-0.71	0.59
Tb								1.00	1.00	0.99	0.98	0.98	0.98	0.98	-0.82	0.89	-0.41	0.91	0.36	-0.88	-0.90	0.04	0.66	-0.70	0.61
Dy									1.00	0.99	0.99	0.99	0.99	0.99	-0.84	0.90	-0.41	0.91	0.34	-0.89	-0.91	0.09	0.63	-0.74	0.63
Ho										1.00	1.00	1.00	1.00	0.99	-0.84	0.93	-0.40	0.89	0.29	-0.90	-0.93	0.11	0.55	-0.75	0.66
Er											1.00	1.00	1.00	1.00	-0.84	0.93	-0.37	0.86	0.25	-0.90	-0.92	0.12	0.50	-0.73	0.67
Tm												1.00	1.00	1.00	-0.84	0.93	-0.37	0.87	0.24	-0.90	-0.93	0.11	0.51	-0.73	0.67
Yb													1.00	1.00	-0.82	0.92	-0.37	0.86	0.22	-0.88	-0.92	0.10	0.51	-0.71	0.66
Lu														1.00	-0.83	0.93	-0.35	0.85	0.21	-0.88	-0.92	0.10	0.50	-0.71	0.66
Mn															1.00	-0.83	0.07	-0.86	-0.52	0.84	0.81	-0.41	-0.56	0.82	-0.80
Fe																1.00	-0.46	0.83	0.26	-0.96	-0.92	0.01	0.37	-0.79	0.61
Al																	1.00	-0.48	-0.24	0.52	0.48	0.47	-0.23	0.39	0.26
Ti																		1.00	0.64	-0.89	-0.91	0.19	0.76	-0.80	0.54
Co																			1.00	-0.44	-0.39	0.29	0.73	-0.56	0.23
Ni																				1.00	0.94	-0.07	-0.43	0.82	-0.56
Cu																					1.00	-0.23	-0.48	0.81	-0.63
P																						1.00	0.12	-0.40	0.66
Th																							1.00	-0.45	0.31
Mo																								1.00	-0.71
W																									1.00

Note: See Table 2.

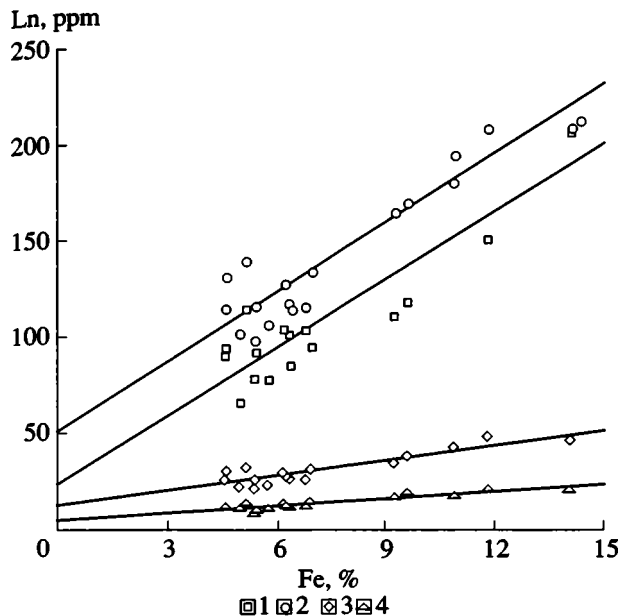


Fig. 6. REE vs. Fe in the radiolarian zone nodules. Supplemented with data in Elderfield *et al.* (1981a). (1) La; (2) Nd; (3) Gd; (4) Er.

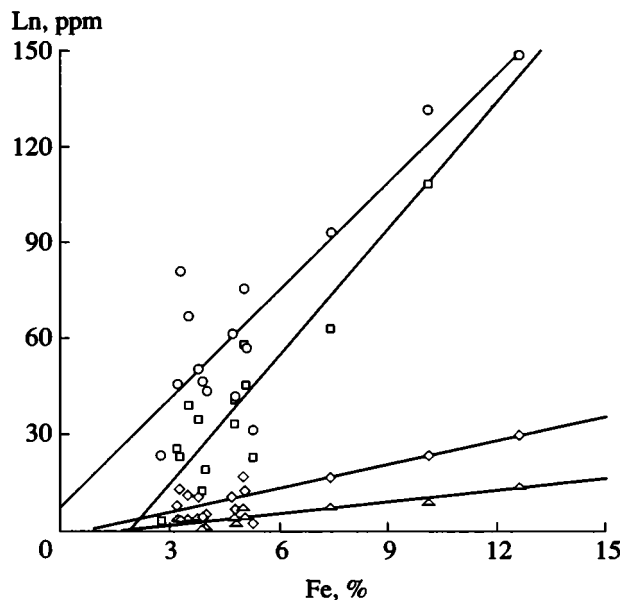


Fig. 7. REE vs. Fe in the radiolarian zone sediments with the introduction of correction for the contents of REE (related to phosphates in sediments) and Fe (related to aluminosilicate matrix). See text for the recalculation procedure. Legend as in Fig. 6.

adsorbed on iron oxyhydroxides and only about 10% P is adsorbed on manganese hydroxides (Balistreri and Chao, 1990).

Previous works demonstrated that the generation of reduced Fe in near-bottom conditions leads to its oxidation and hydrolysis along with active sorption of REE on newly formed oxyhydroxides of Fe(III) from near-bottom waters. Irrespective of the genesis of iron oxyhydroxides, the composition of adsorbed REE mirrors the composition of dissolved REE in near-bottom waters (Dubinin and Volkov, 1989). The phosphate ion sorption from near-bottom waters by iron oxyhydroxides is probably able to intensify the sorption of trivalent REE.

In the oceanic geochemistry of REE, the REE-accumulating capacity of calcium phosphates (apatite) is well known (Elderfield and Pagett, 1986). Evidently, a similar process governs the composition of REE in sediments and diagenetic nodules of the radiolarian zone. Local variations of the REE signature of nodules are caused by local maximums of the organic matter. Increased velocities of near-bottom currents and hilly topography are likely to promote the sorting of suspended material according to the granulometric composition (Bogdanov and Lisitsyn, 1979) even before its precipitation. Generally, larger particles of the organic detritus with abundant organic matter and Fe(II) are precipitated and accumulated on seafloor depressions; this leads to the development of suboxidative diagenesis at local centers.

The suboxidative diagenesis is accompanied by reduction of Mn and its introduction into nodules, oxidation of Fe(II) from the organogenic substance in sediments into Fe(III), and generation of iron oxyhydroxides; the subsequent phosphate ion sorption, in its turn, intensifies the trivalent REE sorption from near-bottom

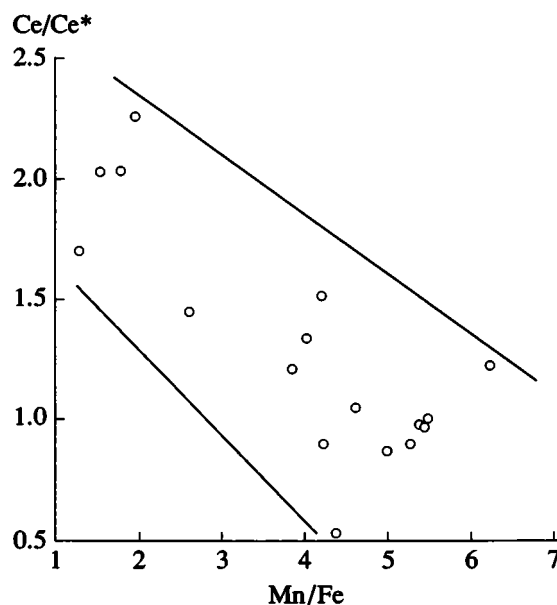


Fig. 8. Ce anomaly (Ce/Ce^*) vs. Mn/Fe in the radiolarian zone nodules. Supplemented with data from Elderfield *et al.* (1981a).

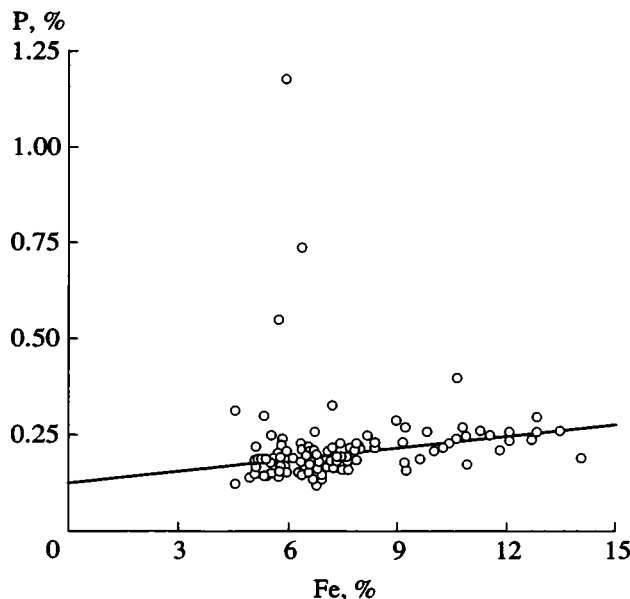


Fig. 9. Relationship between P and Fe in the radiolarian zone nodules. Supplemented with data from (Calvert *et al.*, 1978, 1987; Elderfield *et al.*, 1981a; Calvert and Piper, 1984). Regression equation $[P] = 0.010[Fe] + 0.125$ is obtained from 104 samples. Correlation coefficient = 0.584.

oceanic waters. The introduction of iron hydroxophosphates into diagenetic nodules increases the concentration of P and REE(III) in them and enlarges the negative Ce anomaly (Fig. 8), which is not necessarily associated with the supply of hydrothermal iron oxyhydroxides.

The major part of hydrogenic component of suspension consists of iron and manganese oxyhydroxides and their sorbed complex with positive Ce anomaly, which is formed in near-surface waters (Sholkovitz *et al.*, 1994). The hydrogenic component is smaller than the biogenic counterpart (Bogdanov and Lisitsyn, 1979). As a result of the accumulation of biogenic suspension along sites with minimum near-bottom currents and depressions, its role is suppressed and the hydrogenic suspension becomes predominant in the compositional makeup of sedimentary nodules on slopes and ridges where currents are maximum. The precipitation of this suspension on oxyhydroxide particles is intensified due to the formation of chemical bonds between the hydrogenic particle and sedimentary nodule surface, rather than the gravitational force.

CONCLUSION

(1) The composition and concentration of REE in the radiolarian zone sediments is generally governed by the content of P, which is present as phosphates (bony apatite and iron hydroxophosphates). The study of the reactive part of sediments revealed that 45 to 80% La is concentrated in phosphates. The contribution of HREE in extracts is even higher and is as much as 73–93% for Lu.

(2) In general, rare earth elements in the radiolarian zone nodules are associated with iron oxyhydroxides and hydroxophosphates. We also cannot rule out the possible influence of bony apatite contained in host sediments. The relationship between these phases governs the value of Ce anomaly in the REE signature of nodules. The ratio $Ce/Ce^* > 1$ is typical of sedimentary nodules, whereas $Ce/Ce^* \leq 1$ is common for diagenetic and sedimentary diagenetic varieties. As iron oxyhydroxides are characterized by a positive Ce anomaly, whereas hydroxophosphates and bony apatite are noted by a negative anomaly, one can assume that the latter two phases are accumulated in diagenetic nodules.

(3) The proposed mechanism for the formation of the radiolarian zone nodules elucidates the local variability of their chemical composition. As a result of the elevated bioproductivity of surface waters, a major part of suspended Fe is represented by both oxyhydroxide, Fe(III), and organic detritus-hosted, Fe(II) varieties. If near-bottom currents are present and the ocean floor topography is hilly, relatively large biogenic suspensions are accumulated in depressions where suboxidative diagenesis is developed; this is accompanied by the decomposition of organic matter, oxidation of Fe(II), formation of oxyhydroxides, and sorption of phosphate ion and REE with negative Ce anomaly from near-bottom waters. The finer hydrogenic suspension, which is composed of predominant iron and manganese oxyhydroxides, with REE characterized by a positive Ce anomaly, is precipitated on the oxyhydroxide particle surfaces as a result of the formation of chemical bonds.

ACKNOWLEDGMENTS

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SHORT COMMUNICATIONS

Catagenetic Transformations of Rocks of the Triassic Subsalt Sequence, Algerian Sahara

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Abstract—The Triassic subsalt complex in the Algerian Sahara incorporates highly mineralized (300–400 g/l) Cl–Ca-brines associated with the injection of mineralized waters from overlying saliferous deposits. The metamorphization grade of stratal waters of this complex in the western Triassic Province is one order of magnitude higher than in the eastern part. Such a strong difference in the metamorphization grade of stratal brines within a single hydrogeological complex with waters of a common genesis is attributed to peculiarities of their interaction with host rocks. This paper demonstrates the interrelation between the metamorphization grade of brines and the nature of catagenetic transformations of host rocks and their carbonate–sulfate mineralization that significantly affected the collector properties of sand–siltstone deposits of the Triassic Complex.

INTRODUCTION

We carried out systematic lithohydrogeochemical investigations in the Triassic Province, Algeria, within the framework of the generalization of data on the geological setting and petroleum potential of Algeria; these works were conducted in 1988–1992 by a team of Russian and Belarussian experts according to a contract with the SONATRACH National Company, Algeria.

The object of study is represented by Triassic deposits that are ubiquitous within the so-called Triassic Province and consist of terrigenous, carbonate, halogenous, and volcanogenic rocks. These rocks constitute the predominantly sand–clay, petroliferous complex unconformably overlying the Paleozoic surface at a depth of 1250–5500 m. The total thickness of the complex is as much as 605 m (Fig. 1). It is covered practically over the entire territory by a thick saliferous Triassic–Jurassic sequence.

As a result of the diverse composition and structure of Triassic deposits, absence of fauna, and poor palinological study of sections, there are several local schemes for the differentiation of these deposits. The correlation of lithostratigraphic schemes of Triassic deposits from various regions of the Algerian Sahara is given in Fig. 2.

It should be noted that these deposits incorporate numerous hydrocarbon deposits, including the unique Hassi R'mel gas deposit.

Hydrogeochemical studies revealed that the Triassic Complex contains highly mineralized (300–400 g/l) Cl–Ca-brines of the conventional genetic type related to the injection of mineralized solutions from the overlying saliferous deposits into the Triassic sand–clay deposits and subsequent transformation under stratal conditions (Poroshin, 1981; Kartsev *et al.*, 1989; Makhnach, 1989b). In the western sector of the prov-

ince, within the Tilremt Dome and Wed Miya Depression, the metamorphization grade of stratal waters of the complex is significantly higher than in the Radomes Depression located in the eastern sector (Fig. 3). For example, the metamorphization coefficient of stratal waters, $r_{Ca/Mg}$, is as much as 10–17 in the western sector (boreholes EAA-1, HLJ-2, Af-2, NL-2,3, HR-165) and 0.7–3.1 in the eastern sector (boreholes REH-1,

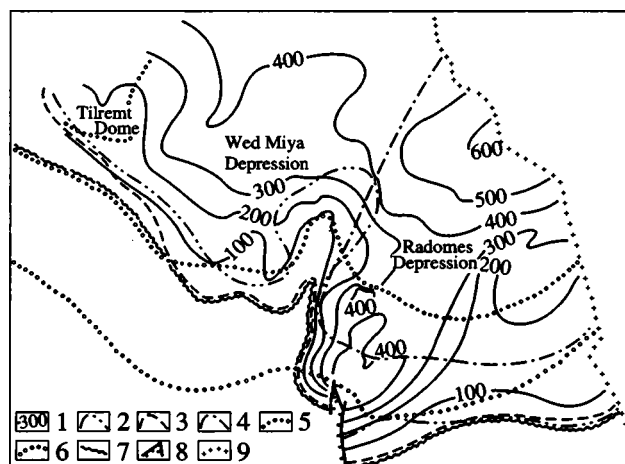


Fig. 1. Schematic map of total thickness of Triassic petroliferous complex in the Algerian Sahara and areal distribution of its lithostratigraphic subdivisions.

(1) Isopachs of Triassic sand–clay (subsalt) complex, m; boundaries of the distribution of lithostratigraphic subdivisions: (2) lower group and analogs, (3) middle and upper sand–clay members, (4) Triassic clay–carbonate deposits, (5) Triassic saliferous sequence (S_1 – S_3), (6) Jurassic saliferous sequence (S_4), (7) southern boundary of the Triassic petroliferous sand–clay complex; (8) tectonic faults; (9) western boundary of Algeria.

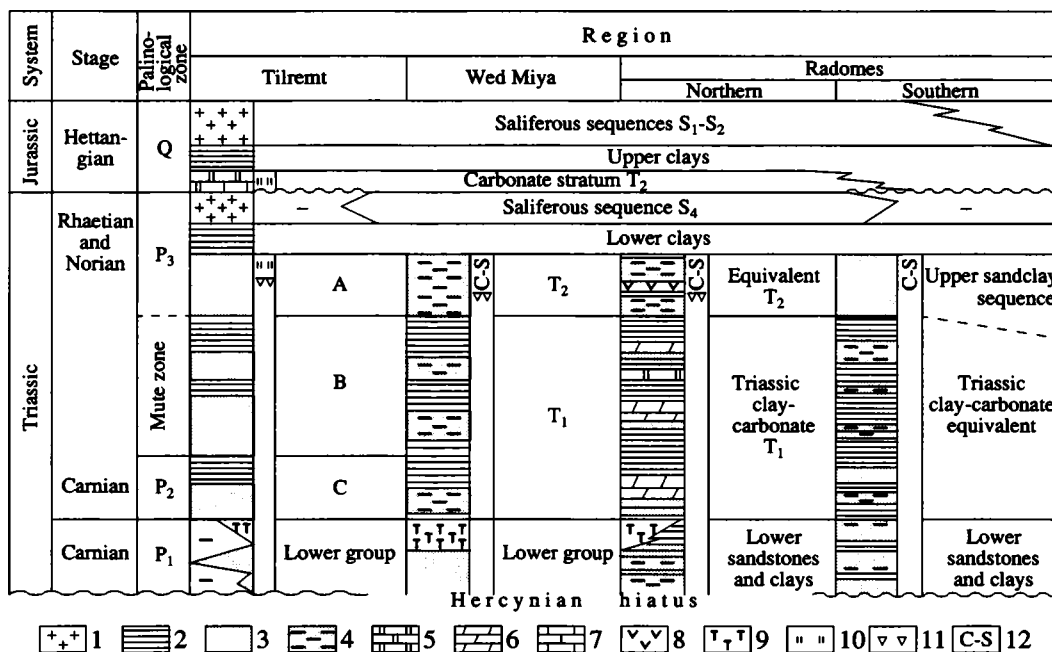


Fig. 2. Correlative lithofacial schemes of the differentiation of Triassic deposits, Algerian Sahara.

Lithological composition: (1) rock salt, (2) clays and claystones, (3) sandstones and siltstones, (4) clayey sandstones, (5) dolomites, (6) marls, (7) limestones, (8) anhydrites, (9) effusive rocks; predominant cement type: (10) dolomitic, (11) anhydritic, (12) clayey-siliceous.

Fm-2, HTB-2, JF-101, etc.). Such a strong contrast in the metamorphization grade of waters within the single hydrogeological complex of a common genesis may be attributed to peculiarities of their interaction within host rocks.

The comprehensive analysis of catagenetic conversions in Triassic sedimentary rocks with the participation of highly mineralized waters reveals that sandstones and siltstones of the central Tilremt Dome differ from their counterparts in other territories; they are characterized by the presence of secondary sulfates and intensive catagenetic dolomitization of all limestone interlayers and carbonate cement. Here, even the thin reference carbonate stratum D₂ located at the bottom of the saliferous sequence is often composed of secondary fine-cavernous dolomite. Some researchers believe that a part of free gas reserves in the Hassi R'mel deposit is related to the aforesaid dolomites.

The secondary crystalline anhydrite usually replaces microcrystalline calcite or infills fissures. The secondary dolomite almost completely replaces calcitic cement in terrigenous rocks.

The wide development of clastic cement and authigenic rocks, which existed here in deposits prior to their catagenetic dolomitization, was probably linked to the elisional stage processes in the Triassic Complex (Kholodov, 1983; Makhnach, 1989a). The lithofacial composition of deposits, which is characterized by a regular alternation of continuous sand (A, B, and C)

and clay strata, promoted the active development of elisional processes (Fig. 2).

The peculiarities of catagenetic transformation of rocks and very high metamorphization grade of associated brines obviously suggest an intensive interaction between the halogenic basin's source brine, which is enriched in sulfates and magnesium chlorides, and the Triassic limestone and calcitic cement according to the Haidinger and Mariniac reactions:



Due to the appreciably lesser content of magnesium sulfate relative to magnesium chloride, the first reaction, which leads to the precipitation of secondary anhydrite, prevailed at the initial stage and promoted a slight deterioration of primary collector properties of rocks. The more intensive and prolonged metamorphization of brines and dolomitization of carbonate cement and calcitic fillings were followed by an expansion of the pore space. Hence, we observe a spatial coincidence of the area of maximum metamorphization of brines with the field of Triassic host rocks characterized by elevated free porosity.

In the central Wed Miya Depression of the Triassic Province, sandy collector-rocks are confined to the Lower (so-called "inferior") group overlain by a thick effusive sequence (Figs. 1, 2); the metamorphization grade of stratal waters is relatively high; and the metamorphization

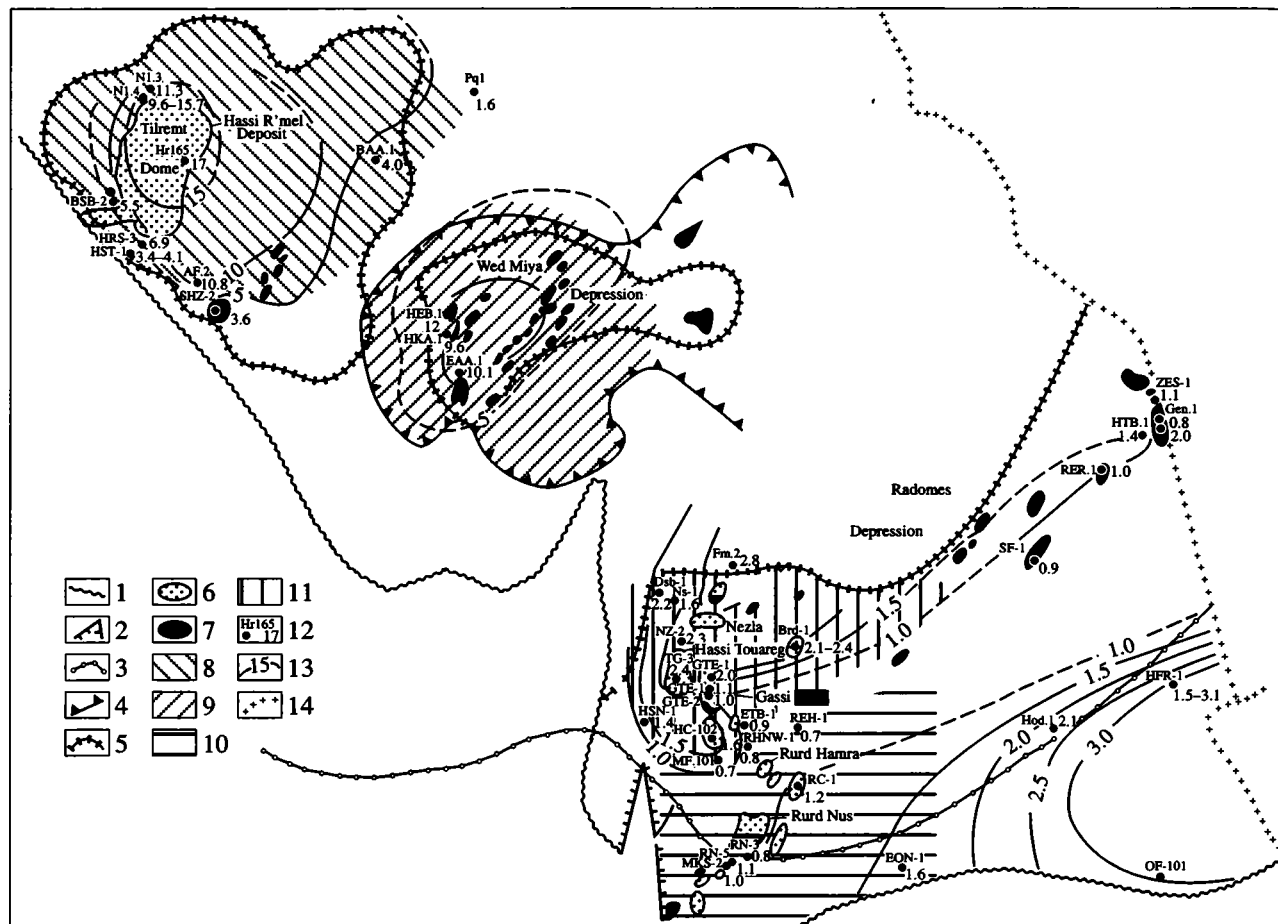


Fig. 3. Schematic lithohydrogeochemical map of the Triassic petroliferous complex, Algerian Sahara.

(1) Southern boundary of the complex, (2) tectonic faults, (3) southern boundary of Jurassic saliferous deposits; (4) boundary of the effusive fluid-resistant sequence of the lower group, Wed Miya Basin; (5) boundaries of Triassic deposits with stronger collector properties; (6) gas pools; (7) oil pools; cement type and its predominance zones: (8) secondary dolomitic (less often, anhydritic), (9) clayey-siliceous and dolomitic, (10) clayey-siliceous without sulfate-carbonate cement and authigenic filling; (11) clayey-siliceous with anhydrite and dolomite inclusions; (12) borehole number (numerator) and metamorphization coefficient, r Ca/Mg, of stratal brines in the Triassic Complex (denominator); (13) isolines of brine metamorphization coefficient; (14) western boundary of Algeria.

coefficient gradually increases from the periphery of effusives, domain toward its interior sector.

Lower group sandstones of the central Wed Miya Depression are distinguished from the Tilremt Dome sandstones by the predominance of siliceous and clayey cement as well as local dolomitization of calcitic inclusions and cement. Secondary anhydrite, which is absent here, is only registered at the effusive sequence pinchout (Fig. 3). These features of the catagenetic transformation of the Lower group rocks and stratal waters in the Wed Miya Depression can be explained in the following way.

The predominantly sandy composition of the studied section and presence of the overlying thick effusive aquifuge restricted the development of elisional processes and calcitic mineralization.¹ Evidently, highly

concentrated brines injected under the effusive sequence of the central Wed Miya Depression beyond the boundary of the above-mentioned aquifuge. The laterally migrating brines reacted at first with the carbonate cement of sand-siltstone beds according to the Haidinger reaction causing removal of sulfates. As a result, in the central part of the depression, the calcitic cement was converted into the dolomitic variety only according to the Mariniac reaction; this promoted the preservation and even some refinement of primary collector properties of rocks in this sector. Hence, we observe the spatial coincidence of the studied sector (with increased porosity of rocks) with the zone of highly metamorphized brines (Fig. 3).

Sand and siltstone strata of other regions of the Wed Miya Depression are characterized by the presence of clayey-siliceous and anhydritic cement with rare inclusions of dolomitic calcite, as well as by the moderate metamorphization grade of brines. Hence, stratal

¹ The calcitic and sulfate mineralization of rocks is understood as pore space filling by secondary calcite, dolomite, gypsum, and anhydrite.

Characteristics of collector properties of rocks, cement types, and metamorphization grade of stratal waters from Triassic petroleum and gas deposits in the southeastern Triassic Province

Deposits	Lower group		Upper group		$r \frac{Ca}{Mg}$	Cement type
	Porosity, %	Permeability, md	Porosity, %	Permeability, md		
Rurd Nus-Rurd Hamra	14.3	238	16.2	365	0.7–0.8	Clayey-siliceous
Gassi Touil	16.5	183	15.0	309	1.1–2.0	Clayey-siliceous, dolomitic, rarely anhydritic
Hassi Touareg	–	–	12.5	140	1.9–2.4	"
Nezla	11.7	13	10.6	110	–	"
North Nezla	10.6	52	8.0	–	–	Anhydritic and dolomitic

waters and rocks here are generally altered according to the Haidinger reaction that led to the precipitation of secondary anhydrite and deterioration of primary collector properties of Triassic deposits.

As mentioned above, stratal waters of the eastern Triassic Province are noted by a low metamorphization grade and increased content of Mg. The carbonate cement is absent in Triassic sandstones and siltstones of brine regions (Rurd Nus and other regions) with minimum metamorphization coefficient (up to 1). Therefore, we can conclude that the interaction between brines and rocks here was very weak; consequently, their influence upon the alteration of primary collector properties was negligible.

Most likely, stratal water regions with relatively higher metamorphization coefficient ($r \text{ Ca/Mg} = 1-3$) were distinguished by a more active secondary dolomitization of the calcitic cement and carbonate rocks according to the Haidinger reaction and precipitation of catagenetic sulfate neomorphs, leading to the deterioration of primary collector properties of Triassic deposits. This inference is corroborated by the following observations: the metamorphization grade of waters increases from Rurd Nus to Gassi Touil, Hassi Touareg, and North Nezla (from south to north), and the predominantly clayey-siliceous cement in Triassic collector-rocks is gradually replaced by the anhydrite-dolomitic cement (see table).

Probably, the regional-scale decrease of porosity and permeability of Triassic rocks of the Upper and Lower groups along the aforesaid direction not only reflects the distribution mode of primary collector properties of rocks, but also indicates the influence of secondary processes. The northward intensification of the Haidinger reaction was responsible for the deterioration of primary collector properties of rocks and the filling of pores by secondary minerals in deposits of the region's northern margin.

CONCLUSION

Hence, our lithohydrogeochemical studies in the Triassic Complex of the Algerian Sahara have indicated that this method can be successfully applied for elucidating specific genetic features of the composition of

stratal waters and investigating the influence of hydrogeochemical processes upon the mode of catagenetic alterations and collector properties of both carbonate rocks (Dmitrievskii, *et al.*, 1987; Makhnach, 1989; Poroshin, 1987, 1990) and terrigenous rocks.

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SHORT COMMUNICATIONS

Celestine Occurrence in Mesozoic Deposits of the Central Ciscaucasia

V. Yu. Alekseev

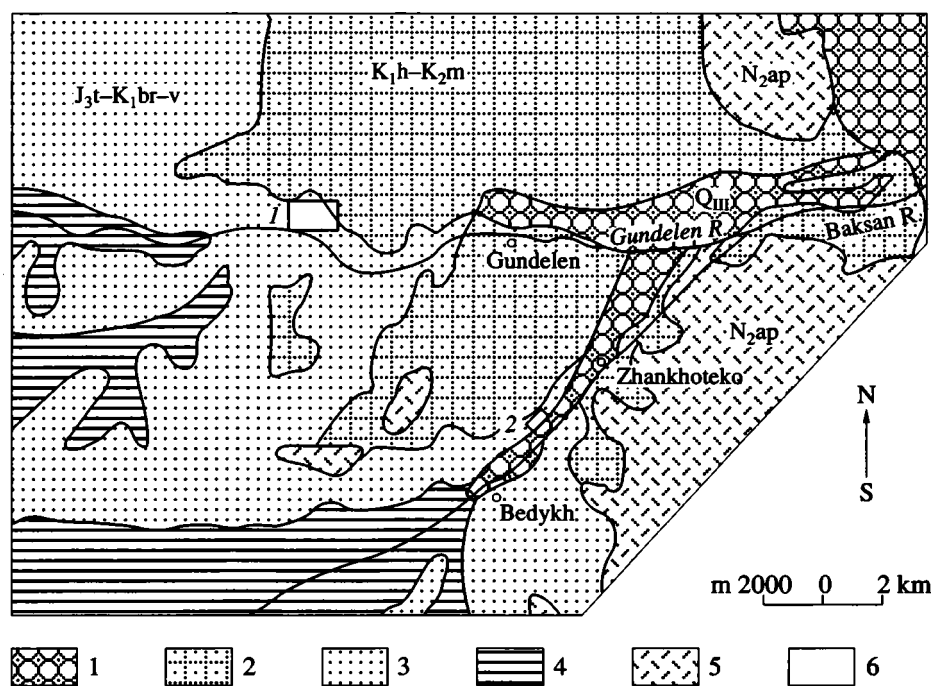
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Abstract—On the left wall of the Gundelen River valley in the Skalistyi Range, North Caucasus, we have registered strontium mineralization over a length of more than 1.5 km. The thickness of productive stratum in the eastern mineralized sector is about 80 m. The mineralization assigned to the contact between Upper Jurassic (Kimmeridgian–Tithonian) and Lower Cretaceous (Berriasian–Valanginian) terrigene–carbonate and carbonate deposits is governed by a sublatral fracture system. The strontium content varies from 633 to 4477 ppm. The maximum concentration of Sr is observed in carbonate rocks.

The structural rearrangement of Ciscaucasia started with the reactivation of ascending tectonic movements at the end of Middle Jurassic. The position of uplifts and depressions was subjected to the strongest changes during the Kimmeridgian–Tithonian time (Buadze, 1989; Koronovskii *et al.*, 1987; Milanovskii *et al.*, 1963; Vishnevskii *et al.*, 1987). This period was characterized by a wide development of saliferous evaporite sequences. Carbonate–evaporite sediments were accu-

mulated in internal-drainage basins restricted by sublatral and anti-Caucasian synsedimentary faults (Buadze, 1989; Burkov, 1980). The resultant hydrochemical regime in depressions and their structural association with the Ciscaucasian petroliferous depressions created favorable conditions for local lead–zinc, barite, and celestine mineralizations along the southern margin of the Ciscaucasian region (Baikov *et al.*, 1974; Buadze, 1989). We registered strontium mineralization



Schematic location of the celestine occurrence at the middle course of the Gundelen River. (1) Quaternary deposits of the Gundelen and Baksan river valleys; (2) Neogene volcanics; sedimentary deposits: (3) Hauterivian and younger (Lower and Upper Cretaceous), (4) Kimmeridgian–Tithonian and Berriasian–Valanginian, (5) Oxfordian and older (Jurassic); (6) celestine occurrences: (1) Gundelen, (2) Zhankhoteko.

Strontium content in Kimmeridgian–Tithonian and Berriasian–Valanginian carbonate deposits of the productive stratum

Sample no.	Brief characteristics of rock and mineralization	Spectral analysis Sr (%)	X-ray fluorescence analysis	
			Ba (ppm)	Sr (ppm)
57	Light-gray organogenic limestone (K_1br-v)	0.04	—	—
56	Dolomitic limestone, locally ferruginous (K_1br-v)	0.04	—	—
17	Limestone; fine celestine dissemination (J_3t)	0.6	304	4477
55	Fine-grained obscure-bedded limestone; celestine dissemination in groundmass (J_3t)	2	140	3903
54	Brownish-gray dolomitic limestone; celestine dissemination in groundmass (J_3t)	8	283	4007
53	Fine-grained, massive dolomitic limestone; fine celestine dissemination (J_3t)	2	128	3527
52	Fine-grained layered limestone; fine celestine dissemination (J_3t)	3	426	3794
51	Limestone, locally brecciated and calcitized; dissemination and fine stringers of celestine (J_3t)	8	555	2511
50	Brecciation and calcitization zone; dissemination and fine stringers of celestine (J_3t)	0.5	101	1364
49	Brecciation and calcitization zone; celestine dissemination (J_3t)	5	228	1668
48	Massive dolomitic limestone; dissemination (J_3t)	1	126	3310
47	Clayey limestone (J_3t)	0.04	<100	633

Note: Based on spectral and X-ray fluorescence analyses (X-ray Spectral Laboratory, IGEM). (—) Not analyzed.

on the left bank of the middle course of the Gundelen River (left tributary of the Baksan River) 7 km upward the settlement of Gundelen (see figure).

The mineralization is confined to the area of Upper Jurassic (Kimmeridgian–Tithonian) and Lower Cretaceous (Berriasian–Valanginian) deposits. Increased contents of Sr (more than 4000 ppm) are observed in the carbonate sequence along the river over a length of more than 1.5 km; the thickness of separate mineralized strata is as much as 80 m; the celestine-enriched layers probably represent a major member of the rock sequence. The upper, significantly carbonate part of the Tithonian section, which hosts the mineralization, is divided into two units: the lower unit is composed of yellowish-gray, fine-grained sandstones with a gypsum coating and sandy-silty limestones; the upper unit consists of alternating layers of organogenic, clayey, and dolomitic limestones. The rocks have light gray, gray, and brownish-gray colors. The structures vary from massive to breccia types. The latter structure, which commonly indicates conformable tectonic fractures, may locally represent epigenetic leaching and collapse breccia, which are widespread in the region (Suletskii *et al.*, 1975).

Based on XRF data, the Sr content in rocks gradually varies from 633 ppm in the lower section to 3527–4477 ppm in the upper section (table). Brecciated zones contain 1600–2500 ppm Sr. Barium, lead, and copper are subordinate, whereas zinc is absent. The irregularly distributed barium does not reveal any distinct correlation with strontium. The barium content is

slightly increased in some samples (see table). Spectral analysis data show lead and copper contents equal to 0.001–0.006%. Mineralized strata, which are megascopically indistinct, can be recognized by increased jointing, breccia structure, and superimposed calcitization. The strontium content in the overlying Valanginian carbonate rocks does not exceed 0.04–0.06%.

The Sr-bearing mineral (celestine) is encountered as fine dissemination and stringers in rocks. Its grain size varies from 0.1 to 1.5–2 mm. In thin sections, it is observed as colorless to white (with yellowish or bluish tint) segregations. It can be divided into two morphological types: the first variety, which lacks distinct crystallographic forms, is found as idiomorphic grains, 0.1–0.5 mm in size; the second variety is observed as tabular crystals up to 2 mm in size. Celestine is characterized by traces of replacement by calcite. The fine-grained variety is generally present in the rock matrix. The coarser, tabular modification, which is encountered in brecciated zones within fine calcite stringers, is probably epigenetic. Its maximum concentration is confined to the contact between fine-grained (<1 mm) matrix and fine- to medium-grained calcite stringers. Celestine is absent in the central parts of stringers.

Taking into consideration the continuity of celestine strata within the outcrops of Kimmeridgian–Tithonian and Berriasian–Valangian deposits in the Gundelen region, their considerable thickness (as much as 80 m), and the fact that a similar celestine mineralization is known 12 km southeast on the left bank of the Baksan River between the settlements Zhankhoteko and Bedyk

(Shvedov and Morozov, 1980), one can assume a wider distribution of celestine mineralization in this region. The mineralization occupies a certain stratigraphic and tectonic position; it is localized along the contact between Upper Jurassic (Kimmeridgian-Tithonian) and Lower Cretaceous (Berriasian-Valanginian) deposits. Celestine is found in all types of rocks, but the maximum concentration is observed in the carbonate member. The Zhankhoteko and Gundelen mineral occurrences are located in sublateral and NE-oriented fracture zones that are emphasized by the Baksan and Gundelen river valleys.

The celestine mineralization serves as a prospecting guide for epigenetic lodes that are considered to be most promising in scale and ore-grade (Baikov *et al.*, 1974; Burkov, 1980). The commercial celestine concentration in this region is possible within the following structures that complicate the monoclinial bedding of Kimmeridgian-Tithonian and Berriasian-Valanginian rocks on the northern limb of Greater Caucasus: (1) regions adjacent to slopes of uplifted blocks (e.g., Mineral'nye Vody block); and (2) regions complicated by regional and local faults, normal faults, and rupture zones. In the territory studied, intersection zones of diverse-oriented fracture systems may also be promising for celestine mineralization.

ACKNOWLEDGMENTS

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CHRONICLE

In memory of Aleksandr Borisovich Ronov

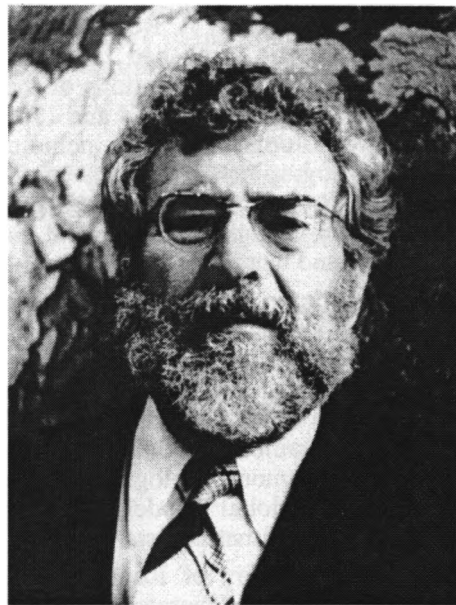
Professor A.B. Ronov, one of the most prominent geologists and geochemists, Academician of the Russian Academy of Sciences, passed away on September 14, 1996, at the age of 83.

A world-known scientist who devoted his life to science has passed away. He was an acknowledged leader in one of the most fruitful scientific directions (evolutionary geochemistry) of the last few years, a passionate advocate for the use of “the number and measure” in the solution of the Earth science problems, and a brilliant researcher in the fields of global lithology, geochemistry, and paleogeography.

Ronov was born on December 16, 1913, in Poltava. After finishing a seven-year school in Khar'kov, where his family had moved to during the period of the so-called new economic policy (NEP), he came to a labor exchange for teenagers and was assigned to an industrial training school of the Khar'kov electromechanical plant. He worked at a plant for two years and was then assigned to a fine mechanics workshop of the Ukrainian Physicotechnical Institute, where he met many prominent physicists. At the same time, he tried to get engaged in literature, published works, and was elected a member of the Association of Ukrainian Writers. But he had selected a geologist's fortune. After a three-year length of service, he was able to continue his studying and was admitted to the Geological Faculty, Khar'kov University, in 1933. In two years, he was transferred to the department of geochemistry, Leningrad University, from which he graduated with honors in 1938. He was appointed as geologist to the staff of the Kovdozero Team of the Leningrad Geological Administrative Department engaged in geological survey and study of the processes of metamorphism in Karelia.

However, as long ago as 1939, thanks to the recommendation of his teachers, academicians F.Yu. Levinson-Lessing and A.A. Polkanov, he was granted a postgraduate scholarship in the Radium Institute, Academy of Sciences of the USSR, created by V.I. Vernadsky, in the laboratory guided by Dr. V.V. Belousov. He studied his supervisor's works on the compilation of maps of facies and thicknesses, and began to think about the possibility of measuring the quantitative parameters using these maps. Consequently, the idea of creation of a volumetric method originated, and Ronov successfully realized this idea during subsequent years. In the spring of 1941, his work seemed to be almost finished.

During the Great Patriotic War, Ronov participated in the prospecting for oil and gas within the Second Baku area. On December 31, 1942, he defended his



Ph.D. dissertation and then started working as a supervisor of the Saratov Expedition of the National Committee on Gas Fuel Industry (Glavgaztopprom), National Commissar Council (Sovnarkom) of the USSR. After the war, he continued prospecting for oil and gas in the Azerbaidzhan expedition of Productive Forces Research Council (SOPS), Academy of Sciences of the USSR; simultaneously, he was involved in research in the field of lithology, paleogeography, and tectonics.

In 1944, Academician O.Yu. Shmidt offered him a D. Sci. fellowship in the Institute of Theoretical Geophysics, Academy of Sciences of the USSR, and in 1948, he defended his D. Sci. dissertation on the subject *The History of Sedimentation and Epeirogenic Movements in the European Part of the USSR*. The volumetric method that formed the basis of further studies by students of his scientific school in the field of quantitative analysis of sedimentary and volcanogenic rock evolution within the limits of vast regions, separate continents, and the Earth's sedimentary shell, was worked out and first used in this dissertation.

In 1950, Academician A.P. Vinogradov invited him to the Vernadsky Institute of Geochemistry and Analytical Chemistry. In 1954, Ronov organized the Laboratory of Sedimentary Rock Geochemistry. His prominent achievements in the development of a wide range of scientific directions are connected with this laboratory. Among them, one of the most significant direc-

tions has been the working out of the theoretical principles of generalization of comprehensive geological data of prospecting and surveying works and reference drilling in the USSR in the form of lithological and paleogeographic maps. Ronov was one of the initiators, supervisors, and active authors of these maps, which were published as a set of atlases for both the European area and the whole USSR (1953–1969).

Beginning in the 1950s, A.B. Ronov together with Academician V.E. Khain published the generalizing global works on lithological formations of the world. This research was completed in 1984 and 1989 by the publication of two volumes of atlases including lithological and paleogeographic maps of the world (continents and oceans). Both regional and global maps have been the basis for quantitative geochemical, lithological, paleoclimatic, and tectonic constructions.

The fundamental empirical estimations of volumes of sedimentary and volcanogenic rocks and sediments of various genesis deposited at different evolutionary stages in large geological structures of each continent and ocean and in the Earth's sedimentary shell as the whole, which were obtained with the use of these maps, aroused great interest among geologists as a real basis for construction of global models by geologists geochemists, and paleoclimatologists.

The most important aim of Ronov and his colleagues was to estimate the masses of chemical elements participating in the formation of large sedimentary basins, tectonic zones, and the Earth's stratisphere at each of considerable stages of geological evolution. This has required many years of hard work, including the collection of thousands of samples of different composition and geological age within the limits of vast regions, characterizing the main types of crustal structures, and their further complex analysis with the use of a unified technique.

These data published by Ronov gained general recognition among geologists of the whole world. But first of all, these data formed the basis for the development of the series of research works started by Ronov and his followers, in which the huge body of factual data was used to study the ways of evolution of lithological, mineralogical, and chemical composition of the Earth's sedimentary shell along with the petrographic and chemical composition of the erosional regions at the continents. These studies established the consistent geochemical trends of change in average compositions of the most important types of sedimentary and magmatic rocks of continents during the geological evolution; these trends are determined by the evolution of composition of the crust-forming abyssal material due to the planet's thermal evolution and the change in the predominant tectonic regime in the Earth's crust.

Ronov created and improved the model of the crustal chemical structure. The estimates of rock masses and compositions were cited and substantiated (Ronov *et al.*, 1990), making it possible to solve a num-

ber of problems of chemical element budget in the Earth's crust. He was deeply concerned about the problems of interrelation and evolution of composition of all the exterior shells of Earth. Together with Academician M.I. Budyko and on the basis of ideas of V.I. Vernadsky, he succeeded in elaborating the quantitative model of change in the oxygen and carbon dioxide contents in the Earth's atmosphere during the Phanerozoic. The book, published together with academicians M.I. Budyko and A.L. Yanshin and containing the substantiation of this model and factual data used for the model calculation, at once became a scientific best-seller and was translated into English, Japanese, and Chinese.

For a long time, Ronov was engaged in another problem—the comparative study of sedimentary rock geochemistry of stable (platform) and active (geosynclinal) tectonic zones. The long-term studies resulted in the discovery of fundamental differences in chemical and mineralogical rock composition, mechanism and scales of element differentiation in different geotectonic zones of the Earth's crust. On the other hand, the surprising similarity in a chemical composition of rocks and tendencies of its evolution within the limits of identical structural zones was found and is corroborated by new data. Many investigations of Ronov and his school on the geochemistry of certain elements (Mn, P, C, elements—hydrolyzates, radioactive and rare earth elements, Li, etc.) in a sedimentary process and geochemistry of stable isotopes of C, S, and O were pioneer works. In each case, the studies carried out made it possible to fill the gap in geochemical knowledge available at that time in the world literature, formed the basis for the calculation of budgets of elements and isotopes in the sedimentary cover and the Earth's crust, revealed the variations in contents and relationships of elements and isotopic composition in the Earth's evolution.

Ronov repeatedly returned to the problems of mineral resources of carbonate and organic carbon and its relation to volcanism, which governed the carbon supply from depths, as a result of which “the law of carbonate accumulation” was extended and deepened, having been supplemented with “the geochemical principle of life conservation.”

At the same time, he periodically discussed the problems of correlation between concentrated (ore) and dispersed elements in deposits, especially in connection with their oil potential.

All these comprehensive projects of A.B. Ronov have been formulated in the distinct concept of geochemical evolution of the Earth's exterior shells, in which various factors, such as tectonic, paleogeographic, abyssal volcanism, and, finally, life, are genetically related, and they form the complex dynamic system of the Earth's biosphere. This concept developed Vernadsky's theory of the biosphere and supplemented it with a great and important empirical significance.

Ronov was one of the most prominent and talented followers of Vernadsky's traditions. His last monograph (*Sedimentary Shell or the Earth's Stratisphere*) published in 1993 reconfirms this.

Ronov enjoyed great recognition in the world geological community. In 1984, he was awarded a Vernadsky gold medal; in 1986, he was elected as an honorary member of the American Geological Society. In 1991, the colloquium *Problems of Lithological and Geochemical Evolution of Sedimentary Rocks* was organized in honour of Ronov at the annual conference of this society. Ronov was awarded a State Prize of the Russian Federation for 1995.

Ronov was a purposeful and courageous man with an unusual working capacity. In spite of physical illnesses, he worked up to his last days: science was his

life. At the same time, he was a versatile, talented man, who liked nature, music, poetry, and life.

His devotion to science always inspired those who worked next to him. His collaborators—disciples and colleagues—will continue and develop the research, to which Ronov passionately devoted the whole his life.

The brilliant and extraordinary image of A.B. Ronov will remain in the memory of all who saw him at least once, in the memory of his friends and colleagues, and his works are destined to live for a long time.

**Editorial Board
of the Journal Lithology and Mineral Resources
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and Analytical Chemistry (GEOKhI)**

CHRONICLE

In memory of Emma Solomonovna Zalmanzon

On September 4, 1996, Emma Solomonovna Zalmanzon, Ph.D. (Geol.–Miner.), head of the Chemical laboratory and oldest researcher of the Geological Institute (GIN), Russian Academy of Sciences, passed away.

Zalmanzon was born on July 11, 1901, in Roslavl', to a dentist's family. Having finished Roslavl's gymnasium, she moved to Moscow and entered the Second Moscow University, which she graduated from in 1926. After the invitation of Prof. K.L. Malyarov, Zalmanzon started working at the Geological Section, headed by Academician A.D. Arkhangel'skii, of the newly created Oil Geological Prospecting Institute (NGRI).

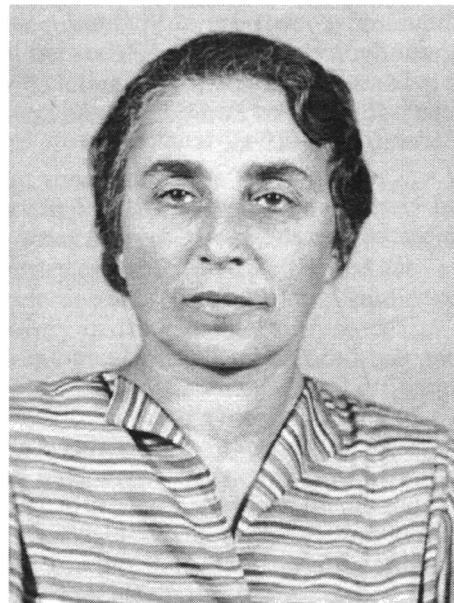
From this time, she was engaged in the comprehensive lithological and geochemical investigations carried out under the supervision of Academician Arkhangel'skii in the Northern Caucasus; she, in collaboration with K.L. Malyarov and S.P. Uspenskii, carried out the complete chemical analyses that formed the basis for the creation of a monograph *Conditions of Oil Formation in the Northern Caucasus* (1927). This monograph was for a long time a guiding link between theory and practice of oil and gas formation in the USSR; this work is still of great importance.

In the early 1930s, Zalmanzon actively participated in the study of the recent and Holocene sediments of the Black Sea, which was carried out under the supervision of Arkhangel'skii and Academician N.M. Strakhov. The comparative lithological studies presented conclusions of extreme importance; in 1930, Arkhangel'skii together with Zalmanzon had published the paper *A Few Words on a Diagenesis of Marine Clay Deposits* in the journal *Doklady Akademii Nauk SSSR*, which anticipated the elaboration of a theory of diagenetic transformations.

In 1934, Zalmanzon was promoted to a position of a head of the analytical laboratory in the Geological Institute, Academy of Sciences of the USSR, which united the Moscow and Leningrad Geological Institutes. From this time until 1974, she was a permanent supervisor of a large group (up to 25–30 persons during the best years) of chemists-analysts.

The series of Strakhov's publications dedicated to the geochemistry of black or combustible shales and bituminous rocks of the Volga region and Russian Platform was closely allied with the work of Zalmanzon's laboratory in the pre-war period.

In the 1940s, during the Great Patriotic War, Zalmanzon, staying in an evacuation in Ufa, organized the work of a group of chemists-analysts aimed at the study



of the Lower Permian halogen deposits of the Ural region; the results were published in a number of journal papers and were used in Strakhov's D. Sci. dissertation. Among these works, the paper *Iron, Manganese, Phosphorus, and Certain Minor Elements in the Lower Permian Halogen Sequence Rocks of the Bashkir Ural Region* (Strakhov, Zalmanzon, Arest-Yakubovich, and Senderova, *Dokl. Akad. Nauk SSSR*, 1944, vol. 18, no. 3, pp. 267–270), is the most widely known. In 1946, Zalmanzon defended her Ph.D. (Geol.–Miner.) dissertation.

Immediately after the war, Zalmanzon was engaged in working out the analytic methods making it possible to determine the forms of occurrence of Fe, S, silica, P, and Mn in sediments and sedimentary rocks. This direction opened new horizons in geochemistry of sedimentary process, because the mineral budget estimation made it possible to precisely characterize geochemical conditions and correlate them with the specific parageneses of minerals and elements.

Results of this work were published in the handbook *Methods of Study of Sedimentary Rocks* (Moscow: GONTI, 1957, vol. II, pp. 5–86), where the most important problems in the field of mineralogy and geochemistry of sedimentary rock formation are disclosed in a number of remarkable papers written by Zalmanzon together with Academician Strakhov.

The monograph of N.M. Strakhov, E.S. Zalmanzon, and M.A. Glagoleva *Geochemistry and Lithology of the Paleozoic Sedimentary Rocks* (Moscow: Akad. Nauk SSSR, 1959), as well as the thematically related journal papers published in the late 1950 should be specially mentioned.

The intensity of chemical weathering at water catchment areas proved to directly affect the distribution of chemical elements at the bottom of paleobasins: the more intense the initial material decomposition, the greater the role of true solutions in a migration of elements, and the deeper the zones of their accumulation maximums, and the more similar are the curves of different elements distribution in a facial profile.

The great laboratory work of Zalmanzon and her chemists-analysts formed the basis of this surprising discovery suggesting that sedimentation is the result of complex interaction between catchment areas and paleobasins rather than of simple chemical reactions in water.

In the late 1960s and the early 1970s, the analytical laboratory of GIN headed by Zalmanzon, supplied with its production a very wide front of geochemical studies. Iron ore and manganese ore deposits (N.M. Strakhov, L.N. Formozova, E.A. Sokolova, and A.A. Gavrilov), bauxites and phosphorites (G.I. Bushinskii, N.A. Lisitsina, N.G. Brodskaya, and V.N. Kholodov), coals and coal-bearing deposits (P.P. Timofeev, V.S. Yablokov, L.I. Bogolyubova, etc.), and volcanogenic sedimentary deposits and associated mineral deposits (I.V. Khvorova,

V.I. Grigor'ev, K.K. Zelenov, and L.N. Botvinkina) were almost simultaneously studied in GIN. Great attention was paid to geochemistry of recent marine and oceanic sediments (N.M. Strakhov, N.A. Lisitsina, and G.Yu. Butuzova), geochemistry of continental lithogenesis (E.V. Shantser, Yu.A. Lavrushin, and A.R. Geptner), and to a number of other problems.

Naturally, all this required a huge number of analytical determinations and tremendous effort of expert chemists.

And, in spite of progressively increased difficulties, the comparatively small analytical laboratory of GIN, under the guidance of calm and always friendly Zalmanzon, was able to cope well with the requests of geologists during a number of years.

The activity of Zalmanzon was repeatedly commended with state awards. She was awarded a medal *For Valiant Labor during the Great Patriotic War*, *Order of Lenin*, and many other medals, and had a title of *Labor-Veteran*.

The talented scientist, intelligent and kind woman passed away from our lives. Our loss is irreplaceable, but we shall ever keep in mind her tender heart and friendly smile.

**The Staff of the Geological Institute (GIN),
Russian Academy of Sciences
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Biochemistry (Moscow)

Editor-in-Chief
V.P. Skulachev

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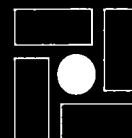
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Editor-in-Chief
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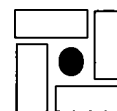
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